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Effects of Natural Organic Matter on Herbicide Adsorption to Activated Carbon

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DIRECTIONS FOR READING THIS THESIS

This thesis is divided into three parts: Part one which is an *Overview*; Part two which is a *Background* and Part three which is a collection of the *Research* reported. Some readers may wish to only get a grasp of the contents of the thesis. You are recommended to start by reading Part one which is an overview of the research carried out and its relevance to current international research. While reading Part one you will notice that references are made to a literature review (Part two section 1, referred to as 2.1) and early experimental work (Part two section 2, referred to as 2.2). Where significant findings are discussed these are referred to Part three which contains the published articles and unpublished manuscripts. There are four of these (sections 3.1 - 3.4) which are listed below. The scope of this thesis covers the mechansims by which natural organic matter hinders the adsorption of herbicides to granular activated carbon. Only drinking water treatment is considered here.

3.1 Edell Å., Morrison G.M., Hedberg T. (1993). Pesticide interaction with activated carbon in the presence of dissolved organic material. *Water Supply*, **11**, 139-148.

3.2 Edell Å., Morrison G.M. Competitive interaction of natural organic matter and herbicides during adsorption to preloaded and non-preloaded granular activated carbon. Manuscript.

3.3 Edell Å., Morrison G.M., Finsrud G., Hedberg T. (1996). Removal of UV-absorbance and TOC characterised NOM in columns of granular activated carbon. In: *Proceedings of Natural Organic Matter Workshop. Influence of natural organic matter characteristics on drinking water treatment and quality.* 18-19 Sept., 1996, Poitiers, France.

3.4 Edell Å., Morrison G.M. Competition of natural organic matter and atrazine for adsorption to preloaded granular activated carbon in drinking water treatment. Manuscript.

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PART 1 OVERVIEW

1.1 The problem: Pesticides, drinking water directives and treatment

Pesticides represent a potential threat to exceedance of increasingly stringent drinking water quality directives (section 2.1). The European Commission (EC) has set acceptable limits called Maximum Admissible Concentration, for pesticides in drinking water where an individual pesticide should not exceed 0.1 μgl^{-1} and total pesticides and low molecular weight organics should not totally exceed 0.5 μgl^{-1} (Sandberg 1992). Table 1.1 summarises several drinking water guidelines.

Table 1.1 Comparison of pesticide regulations in different countries.

Pesticide	US[1] Maximum Contamination Level mgl^{-1}	Canadian[2] Maximum Acceptable Level mgl^{-1}	EC[2] Maximum Admissible Level mgl^{-1}	WHO[2] Guideline Value mgl^{-1}
2,4-D	0.07	0.1	NS	0.001
Endrin	0.002	0.0002	NS	NS
Lindane	0.0002	0.004	NS	NS
Methoxychlor	0.04	0.1	NS	0.001
Pesticide	NS	0.1	0.005	NS
Toxaphene	0.005	0.005	NS	NS
2,4,5-TP	0.05	0.01	NS	NS

NS=no standard; [1] Pontius (1995); [2] Sayre (1988).

Relatively soluble herbicides, such as chlorophenoxy acids and triazines, applied in agriculture can reach drinking water sources. These herbicides show marked seasonal variations in concentration and have longer residence times in groundwater and surface water than was previously believed (Schottler and Eisenreich 1994). Conventional water treatment technologies, such as flocculation/sedimentation, sand filtration, and chlorination are ineffective in the control of pesticides, even if they can have some effect on certain compounds (Miltner *et al* 1989, Lambert and Graham 1995a). The most promising technique for the removal of pesticides in drinking water treatment is granular activated carbon (GAC) filtration or dosage of powdered activated carbon (PAC) (Miltner *et al* 1989). Consequently, emphasis has been placed on understanding removal mechanisms and function of GAC for pesticides under water treatment

conditions. The most common approach has been to carry out Freundlich adsorption isotherms under equilibrium conditions as a basis for predicting treatment efficiency.

1.2 Theoretical background: Freundlich adsorption isotherms and surface heterogeneity

Adsorption isotherms are used to study the adsorption of compounds from one phase to another, for example gas-solid or liquid-solid, at equilibrium. Freundlich developed, at the beginning of this century adsorption isotherms for liquid-solid systems (Freundlich 1906). The Freundlich adsorption isotherm has been found empirically to have a good agreement with adsorption of a range of synthetic organic chemicals (SOC's) to activated carbon from drinking water (Sontheimer *et al* 1988). The Freundlich adsorption isotherm is usually expressed as equation 1 and applies under equilibrium conditions.

$$q=K_F C^n \quad (1)$$

where q is the adsorbed amount to the solid-phase of the adsorbate per mass of the adsorbent and C is the measured concentration of the adsorbate in the solution.

The adsorption isotherm is a plot of log q versus log C and is a straight line if adsorption follows the Freundlich model. The slope is the exponent n, and K_F , the Freundlich constant, is equal to the adsorbed concentration q, when C=1. K_F is related to the adsorbability of the compound studied and n to the surface heterogeneity and therefore the site energy distribution on the surface (Carter *et al* 1992, 1995). The Freundlich adsorption isotherm can also be written as equation 2.

$$q=K_F C^{1/n} \quad (2)$$

The exponent n is generally less than unity and can therefore be written as $1/n$ (Adamson 1990). Here equation 1 has been used. The Freundlich parameters K_F and n are dependent on the initial concentration of the adsorbate and it is therefore important to have the same conditions when comparing different K_F and n values (Sontheimer *et al* 1988). The Freundlich adsorption isotherm corresponds to a heterogeneous surface but there is no assurance that this is necessarily the case when a set of adsorption data fits the Freundlich model (Adamson 1990). Derylo-Marczewska *et al* (1984) and Carter *et al* (1995) have shown that the same adsorption data can fit several adsorption models within a limited concentration range. Examples of other adsorption isotherm expressions are the Langmuir model, empirical extensions of the Freundlich isotherm and combinations of Freundlich and Langmuir (Sontheimer *et al* 1988). However, the Freundlich adsorption isotherm has been found to provide the best description of SOC adsorption to activated carbon and is widely used (Sontheimer *et al* 1988). The usefulness of the Freundlich adsorption model lies in its prediction of the heterogeneous character of the activated carbon surface. Heterogeneous surfaces have a distribution of site energies which can be occupied by the liquid phase solutes and adsorption itself changes the site energy distribution. It has been shown that adsorption of natural organic matter (NOM) to activated carbon results in a loss of surface heterogeneity and that the highest energy sites are preferentially lost (Derylo-Marczewska *et al* 1984, Carter *et al* 1995). This is reflected in the value of the Freundlich exponent n which is significantly less than unity in SOC single solute isotherms and increases when adsorption occurs.

This increase in n demonstrates that the surface is more homogeneous than before. Adsorption of SOC in the presence of NOM either in solution (competitive adsorption) or already adsorbed (preloaded) to the surface leads to a decrease of the adsorption capacity for the SOC, which can be measured as a decrease in K_F, and a loss of high energy sites, seen as an increase in n (Carter *et al* 1992).

The actual mechanism for removal of both SOC's and NOM by activated carbon is an area of active current research, partly because of the emphasis on preventing disinfection by-product formation (Jacangelo *et al* 1995). The adsorption of polar and non-polar organic compounds from solution onto the surface of activated carbon occurs primarily as a result of weak electrostatic interactions (Lambert and Graham 1995b). The adsorption of humic substances is not irreversible as commonly supposed, although because of the slow desorption of humic substances, displacement by SOC can generally be ignored (Johannsen *et al* 1994a). However, humic substances have been shown to affect the kinetics of SOC adsorption by reducing external and internal mass transfer coefficients (Johannsen *et al* 1994b). Lambert and Graham (1995b) have suggested that the higher molecular weight (MW) fractions are preferentially adsorbed on the basis of changes in UV/VIS absorption. This is misleading as humic substance UV/VIS absorption increases with MW. The most likely explanation is that the adsorption potential increases with MW of humic substances due to increasing hydrophobicity and more binding sites per molecule. However, humic substance of a lower MW penetrates deeper into the GAC micropores where there is a greater area available for adsorption. This explains why Johannsen *et al* (1993) observed that the adsorption of humic substances to GAC increases with a decrease in molecular size. Once adsorbed, NOM decreases adsorption capacity by decreasing available surface area and increasing the negative charge on the GAC surface (Newcombe *et al* 1993, Newcombe 1994, Morris and Newcombe 1993).

1.3 Aims and objectives of this study

The aims and objectives of this study were to

* develop analytical methods for the measurement of phenoxy acid and triazine herbicides in water with NOM present.

* examine the adsorption of the selected herbicides to activated carbon in the presence of NOM.

* understand herbicide interaction on the activated carbon surface in the presence of NOM.

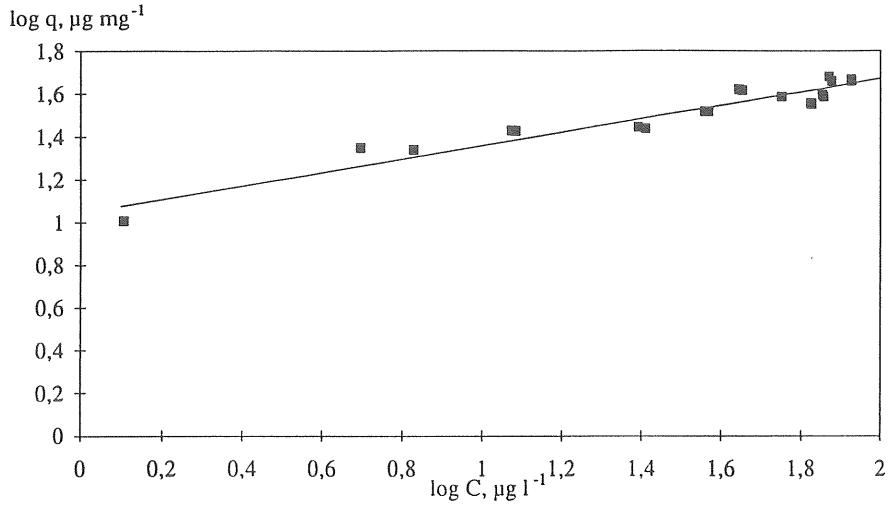
1.4 Competitive effects of NOM on pesticide adsorption: Development of analytical methods and adsorption studies

The studies presented here required the development of extraction methods for the herbicides from water to an organic phase and high-performance liquid chromatography (HPLC) analysis for separation and quantification. At that time, early 1990, solvent extraction and GC/GC-MS

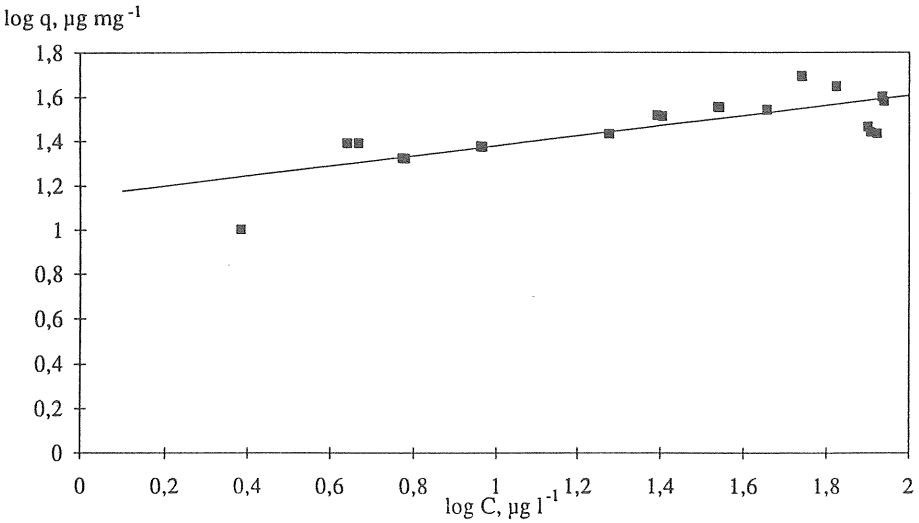
(gas chromatography-mass spectrometry) were still the most used methods for pesticide analysis. Solvent extraction has a number of disadvantages, the most severe is handling of large amounts of organic solvents, usually dichloromethane (Åkerblom *et al* 1990). Solid-phase extraction (SPE) was developed here (sections 2.2, 3.1) as a routine separation of the herbicides atrazine and MCPA from background organics, followed by HPLC with UV detection. This system proved to be flexible as it could be easily adopted for high-performance size-exlusion chromatography (HPSEC) with UV and fluorescence detection at a later date (section 3.4).

Competitive effects of NOM on pesticide adsorption was studied through adsorption experiments carried out in completely mixed batch reactors (CMBR's) stirred with a paddle (section 3.1). Early adsorption isotherms for atrazine and MCPA showed reduction of adsorption capacity in natural waters compared to ultrapure water and curved adsorption isotherms which are an effect of competing organic substances in the solution (section 3.1). Dosage plots were used in place of adsorption isotherms, where the herbicide concentrations at equilibrium in the liquid phase are plotted against the carbon dosage. This plot can be used when the initial concentration of all substances is kept constant and the volume or carbon dose is varied (Sontheimer *et al* 1988). Both the adsorption isotherms (Figure 1.1 and 1.2) and the dosage plots (Figure 1.3) show that MCPA and atrazine are adsorbed to the same extent in ultrapure water, but in lake water MCPA seems to be more sensitive to competitive interaction with NOM. The reason for this is probably due to the difference in chemical structure between atrazine and MCPA. Atrazine is a weak base, but MCPA is an acid and therefore more sensitive to competitive interaction from NOM which also has acidic properties.

Carbon fouling or preloading prior to SOC adsorption is a recognised problem for GAC filters in water treatment (Sontheimer *et al* 1988, Summers *et al* 1989, Speth 1991). Pore blockage and competitive adsorption have been the proposed mechanisms for preloading (Knappe *et al* 1994, Haist-Gulde 1991) and there have been a number of attempts to differentiate the two mechanisms (Carter *et al* 1992, Sontheimer *et al* 1988). Pore blockage is a physical blockage of the pores in the activated carbon which indirectly reduces the available surface for adsorption; competitive adsorption is a direct competition for adsorption sites. Empirically, the difference between pore blockage and competitive adsorption is revealed through their effects on adsorption isotherms and the shifts in the Freundlich parameters n and K_F when NOM is present. Pore blockage gives parallel shifts in the adsorption isotherm, where n remains constant while K_F decreases, whereas competitive adsorption gives non-parallel shifts in the adsorption isotherm and both n and K_F change (Carter *et al* 1992). In fact the identification of a low MW, NOM fraction as the competitive fraction (section 3.4) confirmed that pore blockage is not the dominant mechanism preventing SOC adsorption.



a)



b)

Figure 1.1 Freundlich adsorption isotherms for (a) atrazine and (b) MCPA in ultrapure water.

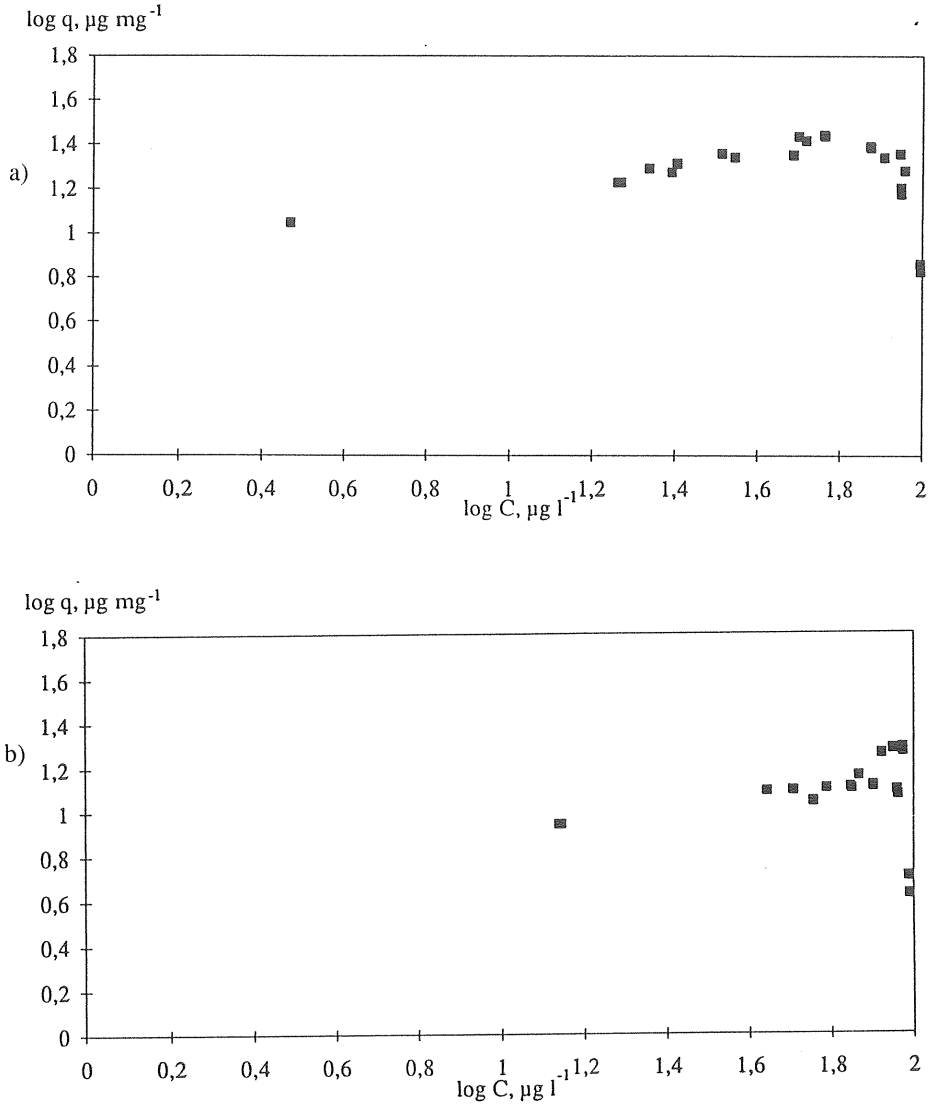


Figure 1.2 Adsorption isotherm for (a) atrazine and (b) MCPA in lake water.

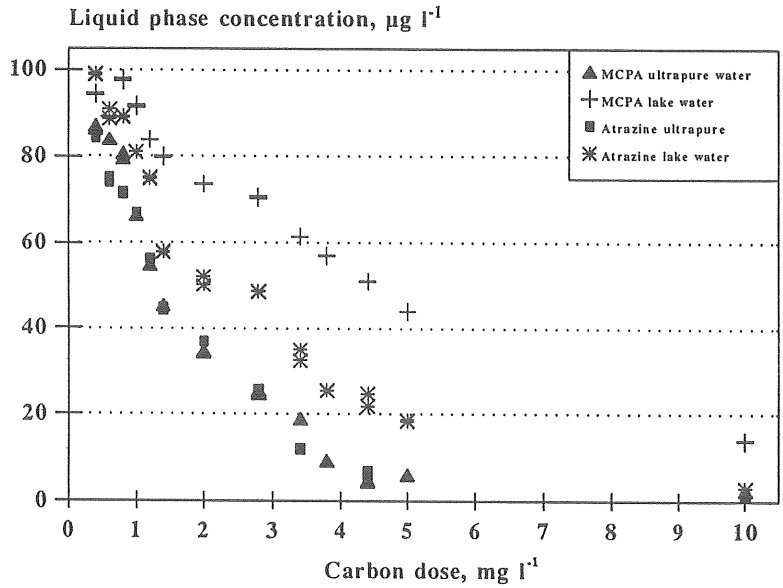


Figure 1.3 Dosage plot for atrazine and MCPA in ultrapure water and lake water.

At the IWSA Specialised conference on Activated Carbon in Drinking Water Treatment (Amsterdam, 27-28 September, 1994) it became apparent that preloading and competitive adsorption are separate phenomena and that experiments should be designed to separate their effects on adsorption. In a follow-on conference (Natural Organic Matter Workshop: Influence of Natural Organic Matter on Drinking Water Treatment and Quality, Poitiers, 18-19 September, 1996), several studies reported (section 3.2, Kilduff *et al* 1996, Newcombe *et al* 1996) on the difference between preloading and competitive adsorption. The latter mechanism was then termed competitive interaction(s). The paper in section 3.2 focuses on preloading and competitive interaction as two different mechanisms. The attempt was to determine the predominant mechanism steering the adsorption of the herbicides, atrazine and MCPA, while considering the theory of site energy distributions. In this study the partition coefficient, K_D, was introduced to demonstrate the effect from preloading and competitive interaction, because of the curved adsorption isotherms previously reported (section 3.1).

K_D represents one point (q/C) in a Freundlich plot and as with K_F, K_D will depend on the initial concentration of the herbicide (Table 1.2). Preloading reduced the K_D in single solute experiments with the adsorption of atrazine and MCPA (Table 1.2). The effect from preloading is also clearly demonstrated in Figure 1.4 where the difference between the profiles for non-preloaded and preloaded carbon in the low dissolved organic carbon (DOC) region represents the effect from preloading. Competitive interaction was studied through NOM dilution experiments with non-preloaded GAC and preloaded GAC (Figure 1.4).

Table 1.2 Single solute partitioning for non-preloaded and preloaded GAC and different herbicide concentrations.

	K_D, lmg^{-1}	
	Non-preloaded	Preloaded
Atrazine (μgl^{-1})		
10	14	7.6
100	4.9	2.9
MCPA (μgl^{-1})		
10	8.5	5.5
100	1.9	0.7

For both atrazine and MCPA, NOM competed significantly at raw water concentrations (~5 mgl^{-1} DOC) (Figure 1.4). The K_D of atrazine increased gradually with NOM dilution, while no significant increase in K_D for MCPA was found until NOM dilution reached almost equimolar concentrations. The competitive interaction from NOM intensifies with an increase of DOC, although even at a DOC concentration below 1 mgl^{-1} competitive interaction overrides the effect from preloading. The results can be explained by the site energy distribution theory (Carter *et al* 1995), where activated carbon has a heterogeneous surface with a distribution of adsorption site energies and where the sites with the highest energies are occupied first. Assuming irreversible adsorption on the preloaded GAC, NOM adsorbs to these high energy sites and reduces the adsorption capacity for the herbicides. Adsorption then follows at sites with lower energies where NOM and herbicides compete for the sites. Consequently, for drinking water treatment, competitive interaction seems to be more critical in reducing the removal of herbicides than preloading with NOM. Preloading will cover adsorption sites, but there are still sites available for herbicide adsorption. These findings are supported by previous pilot plant studies by Speth (1991), where a significant reduction of adsorption capacity was found when NOM was preloaded in the absence of SOC compared to the effect of NOM during actual adsorption.

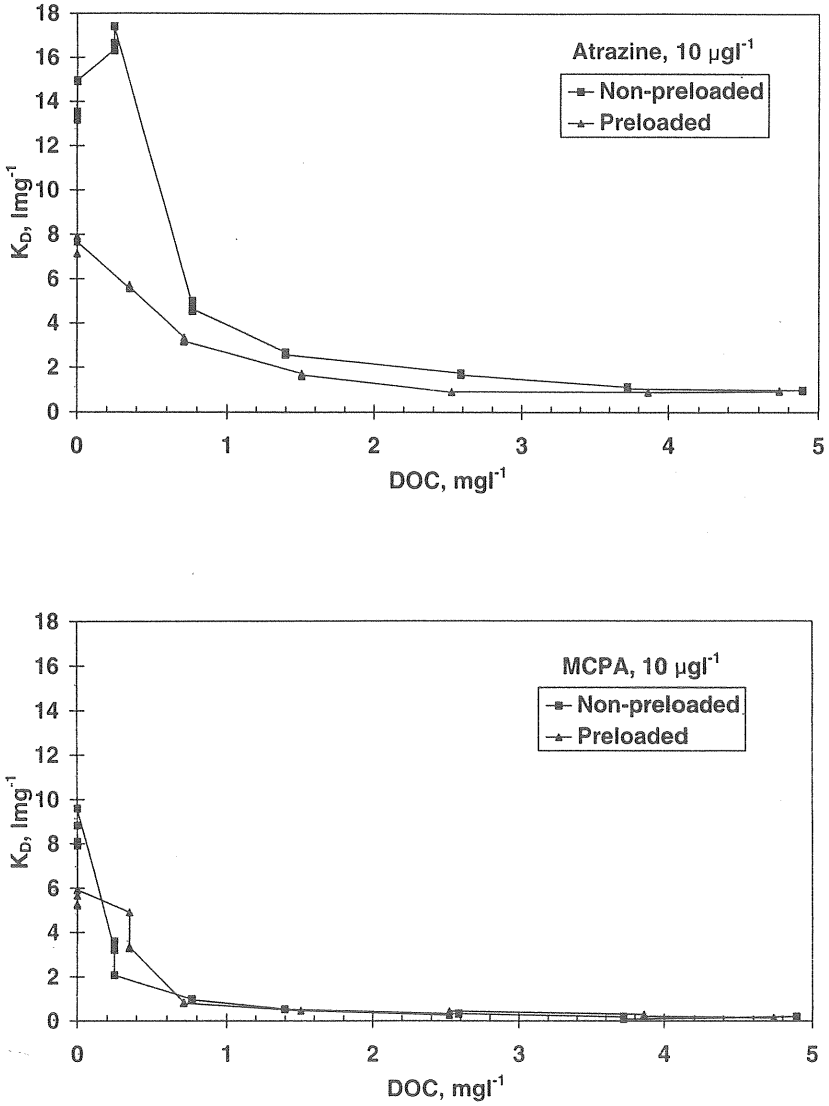


Figure 1.4 NOM dilution curves for atrazine and MCPA at preloaded and non-preloaded GAC.

1.5 Towards a characterisation of competing NOM in pilot columns

In the paper in section 3.3, NOM is characterised as total organic carbon (TOC) and as UV absorbance at three wavelengths 254, 265 and 280 nm. The wavelength of 254 nm is commonly used for the indirect measurement of aquatic humic substances, although the choice of wavelength is operational because it corresponds to the sharp spectral line of a low-pressure mercury lamp (Dobbs *et al* 1972). Wavelengths of 265 and 280 nm are used for the semi-quantitative analysis of lignin-type substances in water (Lawrence 1980). Specific UV absorbance (SUVA) was also used in this study for the characterisation of NOM. SUVA is defined as the ratio of UV absorbance, usually but not necessarily UV_{254} (Krasner *et al* 1996), to the TOC content and is expressed as $(m^{-1})(mgl^{-1})^{-1}$. Empirically it has been shown that higher SUVA values (4-5) correspond to more hydrophobic, aromatic aquatic humic substances with a high MW of NOM compared to lower SUVA values (< 3) which are largely of non-humic character, more hydrophilic and less aromatic in structure (Edzwald and van Benschoten 1990). Our investigation was carried out in pilot-scale GAC columns, equipped with sampling ports along the bed depth to provide SUVA profiles through the whole column. The SUVA profiles demonstrate the preferential removal/adsorption of the UV_{254} component of NOM compared to TOC characterised NOM down the GAC column (Figure 1.5).

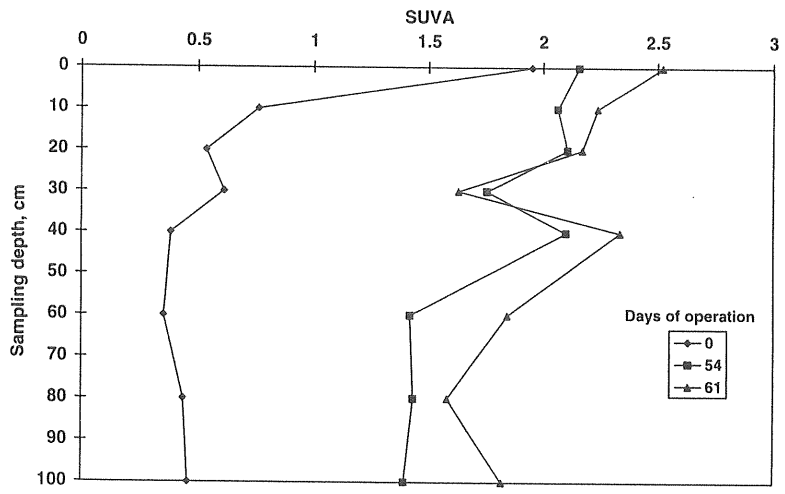


Figure 1.5 SUVA profile for pilot-scale GAC column with a 30 minute empty bed contact time (EBCT).

No difference was observed in the SUVA profiles for the other selected wavelengths which indicates that humic substances (UV_{254}) are removed to the same extent as lignin-type substances (UV_{265} and UV_{280}). The competitively adsorbing component observed here through the SUVA

profiles is probably the small, hydrophobic aromatic substances of NOM. The interesting result obtained here for the preferred removal of UV-absorbing NOM led us to consider the combined effect of molecular size and spectral characteristics on competitive interaction.

1.6 An explanation of preloading and competitive interaction for atrazine adsorption to GAC in drinking water treatment

More detailed information for the competing NOM fraction was provided by high-performance size-exclusion chromatography (HPSEC) where the lower MW fractions seem to be responsible both for preloading and competitive interaction (section 3.4). HPSEC with UV and fluorescence detection was used to examine the MW distributions in treated and untreated surface waters and groundwater without any concentration or fractionation step prior to HPSEC analysis. Lower MW fractions are not removed in drinking water treatment as shown by HPSEC-UV chromatograms (Figure 1.6) and this fraction is also present in the groundwater used in the study (Figure 1.7). Chin *et al* (1994) have also shown that NOM is less polydisperse and smaller (MW 840 - 2 300) than previously proposed and should therefore penetrate into the deeper GAC micropores. The persistence of this fraction through water treatment processes explains why preloading is observed in GAC columns, even though GAC is frequently the penultimate process before pH-adjustment and disinfection.

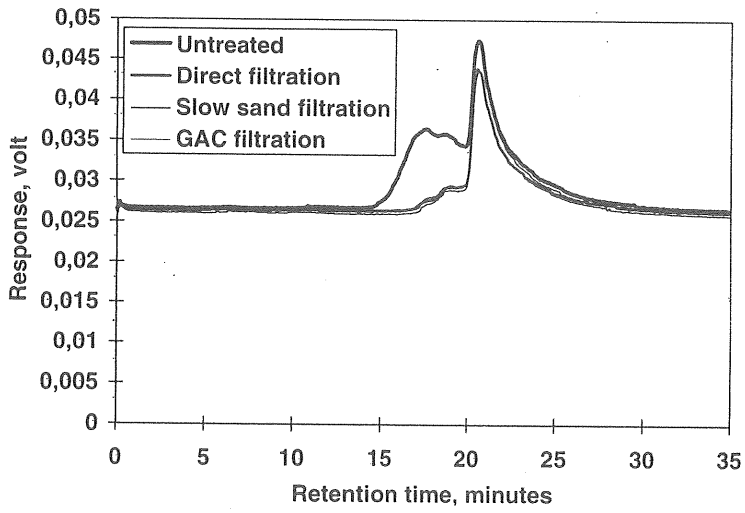


Figure 1.6 HPSEC-UV chromatograms of NOM in untreated and treated water through the Finnsjön water treatment plant.

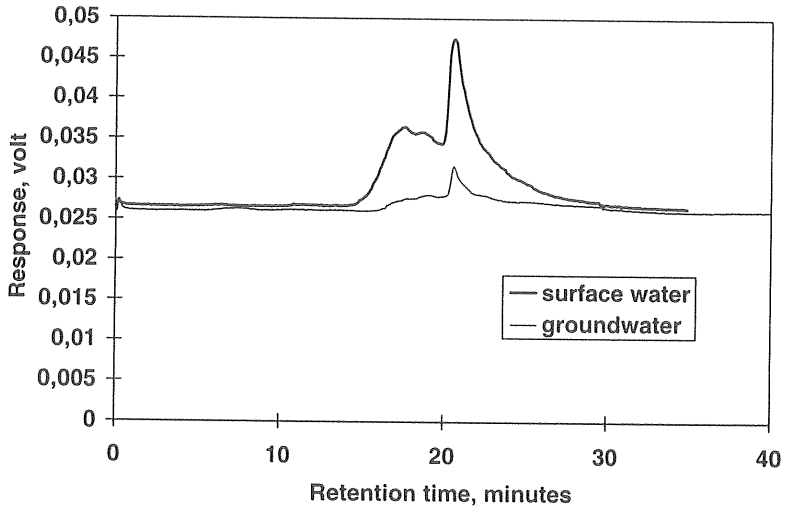


Figure 1.7 HPSEC-UV in Gräfsnäs groundwater and lake Finnsjön (surface water).

The adsorption studies reported in section 3.4 show the effect of preloading and competitive interaction of NOM on atrazine adsorption for crushed and preloaded GAC. The preparation of preloaded GAC for Freundlich adsorption isotherms is difficult, because when GAC is crushed to allow rapid equilibrium of SOC with adsorption sites, fresh non-preloaded adsorption sites can be exposed (Carter *et al* 1992). In this study (section 3.4) the GAC was therefore crushed in a mortar, sieved and the fraction of 74-125 μm was then preloaded in minicolumns with different water qualities. This procedure differs from previous studies (section 3.2), where adsorption experiments were carried out after preloading in pilot-scale filters and crushed after preloading to <63 μm. A reference preloaded GAC was prepared to allow comparison of competitive interaction under the same preloading conditions. Adsorption isotherms for atrazine were carried out with reference preloaded GAC in different background waters, ultrapure water, lake water, groundwater and with polystyrene sulphonate (PSS) standards present. The preloading and competitive effects through the two treatment plants, Lackarebäck (lake Delsjön source) and Finnsjön (lake Finnsjön source), were studied. This was done by preloading GAC in minicolumns with the NOM in the untreated or treated water for the treatment step under investigation and this GAC was termed site-preloaded.

The effect of preloading GAC with NOM and the competitive interaction of NOM on atrazine adsorption is revealed through comparison of n values (Figure 1.8a) and K_F values (Figure 1.8b). In these experiments, reference preloaded GAC was used in combination with the different background waters. Site energy distribution, as indicated by n, was not significantly affected by preloading with NOM in the minicolumns. It is known that extended preloading can lead to an increase of n towards unity, due to the occupation of high energy sites (Carter *et al* 1992, 1995). This effect is observed for the competitive interaction of Delsjön NOM with atrazine at fresh GAC adsorption sites (Figure 1.8a). However, the general effect of a competing substance on atrazine adsorption is a reduction in n; this is observed for the PSS standard of low MW and

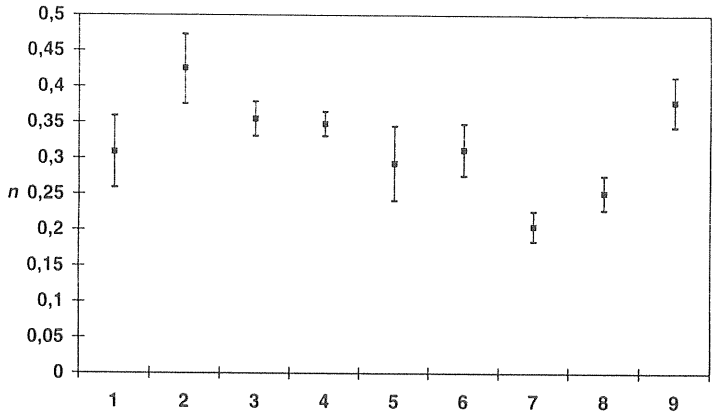
Delsjön NOM. The probable mechanism for competitive interaction is that the excess of NOM or PSS 1 430 adsorbs to the whole range of available sites. This leads to a shift to lower n values and also explains the significant reduction in K_F (Figure 1.8b). Although preloading does lead to a lowered K_F value for atrazine in the absence of competing substance (Figure 1.8b), the effect of a background NOM (competitive interaction) is always overriding, whether for fresh or preloaded GAC. The PSS 1 430 standard shows a significantly reduced K_F for preloaded GAC, however, both Gräfsnäs and Delsjön NOM show a greater effect on K_F. This finding confirms that the low MW, NOM fraction separated by HPSEC is responsible for competition, as the PSS standards > 1 430 show no effect. There appears to be no evidence of pore blockage by larger molecules during atrazine adsorption to GAC.

The low DOC concentration for the groundwater (0.55 mgl^{-1}) underlines previous findings (section 3.2) for dilution experiments that competitive effects are observed down to equimolar concentrations of the target analyte and competitive substances. The question remains whether competitive effects of NOM remain through a water treatment plant.

The reference preloaded GAC served as a control with the same preloading conditions for studies of the additional effect of competition of NOM and atrazine through the two drinking water treatment plants (WTP). The results are shown in Figure 1.9 (Lackarebäck) and Figure 1.10 (Finnsjön). Ultrapure water illustrates the effect of preloading alone and should be compared to the untreated and treated waters, which show the additional competitive interaction from NOM. For both treatment plants it can be concluded that the extent of competitive interaction is not significantly reduced during water treatment. Low atrazine removal can be attributed to competition with the low MW fraction, which was found by HPSEC to be poorly removed during water treatment (Figure 1.6).

The low MW, NOM fraction does though, appear to have a significant effect on both the preloading phenomenon and competition during adsorption.The effects of preloading and competitive interaction can be separated by the use of site-preloaded GAC adsorption experiments with ultrapure water and site sampled water (Table 1.3). In this case the ultrapure water shows the effect from preloading within the treatment plant. The additional effect from competitive interaction is revealed in adsorption experiments where site-preloaded GAC is combined with the site sampled water. The effects from preloading and competitive interaction are slightly elevated for the untreated water from both treatment plants compared to the treated waters but there is no significant difference between the treatments through both WTP's (Table 1.3). This indicates that the high MW fraction could be responsible for some of the effects from preloading and competitive interaction in untreated water but that the low MW fraction separated by HPSEC, and which is found at all treatment steps, determines both preloading conditions and competitive interaction.

a)



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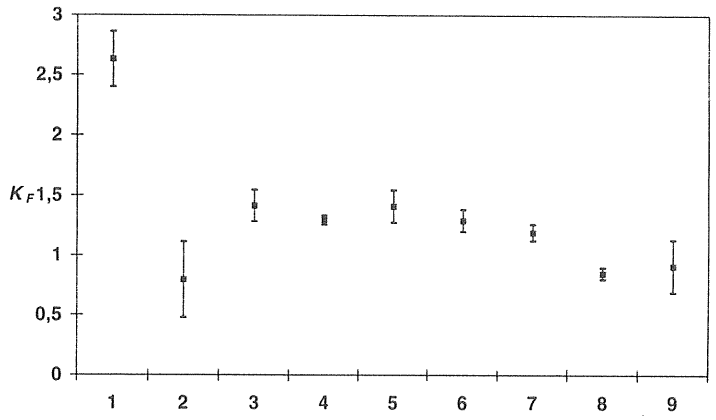

No	GAC conditions	Background water
1	Fresh	Ultrapure
2	Fresh	Delsjön
3	Preloaded, reference	Ultrapure
4	Preloaded, reference	PSS 16 800
5	Preloaded, reference	PSS 6 780
6	Preloaded, reference	PSS 4 300
7	Preloaded, reference	PSS 1 430
8	Preloaded, Gräfsnäs	Gräfsnäs
9	Preloaded, Delsjön	Delsjön

Figure 1.8 Variation in (a) n and (b) K_F with preloading and background competing substance. The 95% confidence intervals are shown with a square representing the mean of four samples.

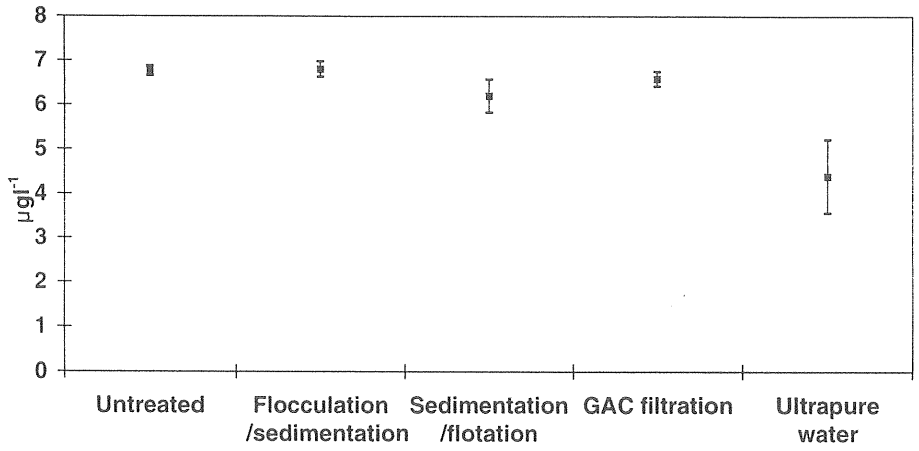

Figure 1.9 The removal of atrazine (10 μgl^{-1}) by reference preloaded GAC through the Lackarebäck WTP. The 95% confidence intervals are shown with a square representing the mean of four replicates.

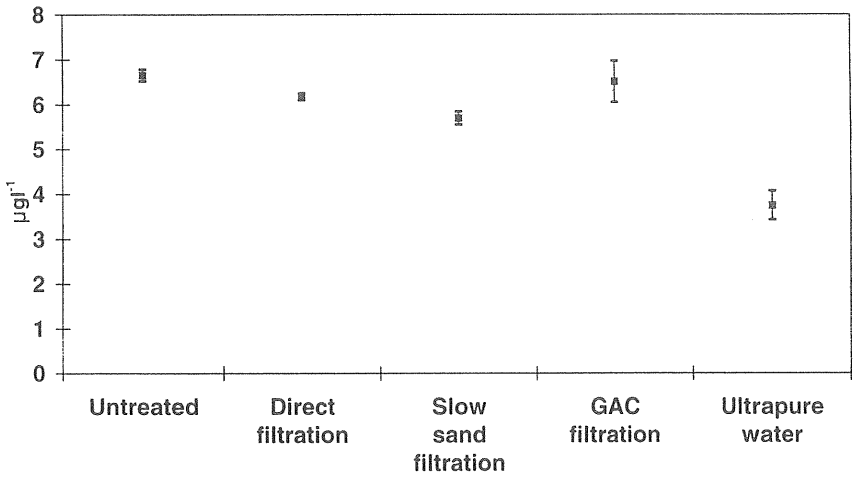

Figure 1.10 The removal of atrazine (10 μgl^{-1}) by reference preloaded GAC through the Finnsjön WTP. The 95% confidence intervals are shown with a square representing the mean of four replicates.

Table 1.3 Effect of preloading and competitive interaction on atrazine adsorption to site-preloaded GAC through the Lackarebäck WTP and Finnsjön WTP. The mean atrazine concentration for four replicates is presented with the 95% confidence interval in parenthesis. The initial concentration of atrazine was 10 μgl^{-1}.

Treatment plant Site	Site-preloaded GAC Ultrapure water Atrazine concentration, μgl^{-1}	Site-preloaded GAC Water at site Atrazine concentration, μgl^{-1}
Lackarebäck		
Untreated	3.7 (3.6-3.8)	6.7 (5.9-7.6)
Flocculation/sedimentation	2.8 (2.5-3.2)	5.7 (5.6-5.9)
Sedimentation/flotation	3.5 (3.4-3.6)	5.8 (5.2-6.5)
GAC filtration	3.3 (2.6-4.0)	5.7 (5.1-6.4)
Finnsjön		
Untreated	3.7 (3.4-4.1)	7.2 (6.8-7.7)
Direct filtration	2.4 (2.3-2.5)	6.3 (6.2-6.4)
Slow sand filtration	1.6 (1.6-1.7)	5.8 (5.6-5.9)
GAC filtration	2.2 (2.0-2.3)	5.3 (5.0-5.5)

Clearly, the competitive interaction of NOM with herbicides has a significant effect on adsorption to preloaded GAC and values reported for distilled water provide an overestimation of K_F and n values. Prediction of GAC performance in a treatment plant for herbicide removal therefore requires a consideration of both NOM preloading and NOM competitive interaction. For the most satisfactory prediction the selected GAC to be used should be precrushed and site-preloaded and adsorption isotherms for target analytes carried out in the presence of the relevant NOM.

1.7 Future perspectives

Pesticides continue to represent a threat to exceedance of increasingly stringent European water quality directives and GAC continues to represent the Best Available Technology for pesticide removal in drinking water treatment. Current international research, including the findings reported here, demonstrates that a low MW refractory NOM fraction accounts for competitive effects during GAC adsorption and that this fraction is not affected by conventional water treatment.

Further improvement in the design of GAC filters to allow the preferential adsorption of pesticides or the reduction of NOM interference seems an unproductive approach, because the competing fraction is always in excess of target analytes, even in groundwater. Alternative

technologies have been proposed for the removal of NOM, based on either biodegradation (slow sand filtration) or filtration (membrane filtration). A biodegradation alternative is not particularly promising for the removal of the competing NOM fraction as the low MW fraction is refractory. However, for readily degradable pesticides a direct removal by slow sand filtration may prove satisfactory (Lambert and Graham 1995a). The higher MW, NOM fraction is readily removed during water treatment and may well provide the basis of biodegradable dissolved organic carbon (BDOC). Membrane filtration does though provide an interesting alternative. Removal of the low MW, NOM fraction would require nanofiltration rather than ultrafiltration and nanofiltration could be followed by GAC removal. Pioneering studies by Duguet *et al* (1993) have shown that this approach is effective in removing pesticides in drinking water treatment and nanofiltration-GAC is therefore well poised to solve the competitive effects presented in this thesis.

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PART 2 BACKGROUND

2.1 Pesticides in the environment and their removal from drinking water

There is an increasing and justified concern over the occurrence of pesticides in the aquatic environment and their potential presence in drinking water. This concern has resulted in extensive monitoring programmes for determining the dispersion and persistence of pesticides, as well as a focus on drinking water technologies to remove variable and low pesticide concentrations.

2.1.1 Pesticide use and the environment

Pesticides will be defined here in terms of chemicals used in agriculture for the eradication of unwanted organisms. Herbicides, insecticides and fungicides are the most important groups of pesticides in agriculture. In each of these groups there are different chemical substance groups that have an effect on target organisms. Phenoxy acids and triazines are important herbicides, organophosphorus containing compounds and chlorinated hydrocarbons are widely used as insecticides, and dithiocarbamates dominate among the fungicides.

The total amount of pesticides sold in Sweden has decreased during the last ten years (Table 2.1). The phenoxy acid MCPA is one of the most used herbicides in Sweden, with 111 tons sold in 1995 (Kemikalieinspektionen 1996).

Table 2.1 Use of herbicides, insecticides and fungicides in Sweden (Berggren 1989, Kemikalieinspektionen, 1991, 1994, 1996).

	Pesticides used (ton pure substance)		
	Herbicides	Insecticides	Fungicides
1972	3947[1]	206	436[2]
1982	4234	232	716
1988	2238	159	679
1990	1743	76	610
1993	1273	52	283
1995	1148	45	181

[1] Including plant growth regulators
[2] Including seed dressings

2.1.2 Persistence of pesticides

The knowledge of the persistence of pesticides is important for determining whether they are likely to reach raw water before degradation occurs. The time for the concentration of a pesticide to decrease by 50 percent is generally referred to as chemical persistence (Torstensson, 1988) and is calibrated through controlled laboratory experiments. More relevant in agricultural terms is the phytotoxic persistence of the pesticide (Table 2.2) which is defined as the time between application to the soil and crop sowing without risk of crop damage (Torstensson, 1988). Phytotoxic persistence is measured in the field and depends on the crop to be cultivated.

Table 2.2 Chemical and phytotoxic persistence of selected herbicides (from Torstensson, 1988).

	Persistence, days	
	Chemical	Phytotoxic
MCPA	7-28	7-28
TCA	130-365	130-365
Diquat	> 365	< 7
Glyphosate	130-500	7-14

For certain substances such as diquat and glyphosate, toxicity to crops decreases rapidly after application, allowing sowing (Table 2.2). These substances are still chemically present but are probably adsorbed to the soil so that they are no longer bioavailable. The degradation of pesticides occurs through physical, chemical and biological processes (Coats 1991). Even though the initial pesticide disappears, the degraded products may remain and in some cases, e.g. organophosphorus insecticide residues, retain toxicity (Torstensson 1988).

Chemical persistence is of more concern than phytotoxic persistence when investigating the possible contamination of ground and surface waters, as phytotoxic persistence is only relevant to agricultural science. A distinction should also be made between soil persistence and water persistence. It has been shown that the half-life of atrazine in soils is 21-58 days (Schottler *et al* 1994) or 60 days (Pereira and Rostad 1990) being converted to the metabolite desethylatrazine, while the half-life in lakes is estimated as months to years (Schottler and Eisenreich 1994).

2.1.3 Pesticide transport

After application pesticides can be transported, *via* particles, in surface runoff or into the atmosphere through wind and soil erosion. Chemical persistence in the environment may differ from controlled laboratory studies due to degradation conditions.

2.1.3.1 *Atmospheric transport*

Pesticides in the atmosphere can be washed out in rainfall, the extent of this process depending on soil handling, climate and topography. Trace concentrations of triazine herbicides have been found by Buser (1990) in rain and snow samples (Table 2.3). The data in Table 2.3 also reflect seasonal variations since the triazines could not be detected in snow samples. The detected concentrations are in the same range as other reported values. Richards *et al* (1987) found atrazine in a concentration range of 0.1 to 1.0 μgl^{-1} and simazine at 0.1 to 0.5 μgl^{-1} in rainwater in the northeastern United States.

Table 2.3 Concentrations of triazines in rain and snow at different locations in Switzerland (Buser 1990).

Sampling location	Concentration, ngl^{-1}		
	Atrazine	Simazine	Terbutylazine
Wädensuil	nd-193	nd-47	nd-87
Zürich	2.8	1.2	21
Bachtel	2.5	1.3	0.5
Lägern	nd-600	nd-121	nd-198

nd = not detected

2.1.3.2 *Mobility of pesticides in soil*

Pesticides that come in contact with soil can either be adsorbed or follow the movement of water through the soil profile. The transport of pesticides through soil depends on factors connected to the soil; type, content of organic matter, pH, cation exchange capacity, water holding capacity, and to the pesticides; water solubility, dipolar structure and acid-base behaviour (Somasundaram *et al* 1991). Tile drain and lysimeter values gave atrazine concentrations of 0.5-20.5 μgl^{-1} for agricultural soils (Jayachandran *et al* 1994).

Several attempts have been made to classify the potential of pesticides for soil transport. For example, Torstensson (1988) classified individual pesticides from 0 (totally soil adsorbed) to 3 (totally water soluble) with additional information on K (general soil adsorption coefficient) and K_{OC} (K/organic content of soil). Other methods for determining pesticide soil mobility include soil thin layer chromatography (Helling and Turner 1968) and the use of mathematical models (Seiber 1987). Mathematical models are usually based on hydrogeological data and parameters which indicate the probability that an individual pesticide will reach groundwater (Aller *et al* 1986).

2.1.4 Pesticides in surface water and groundwater

The low concentrations and difficulty of pesticide analysis in natural waters limits the possibility for the detection of pesticides in raw water sources. However, drainage channels for agricultural runoff provide concentrations high enough for the study of optimal applications to prevent leakage. Kreuger and Brink (1988) found eleven herbicides, five insecticides and two fungicides in agricultural runoff in southern Sweden. Pesticides were also detected outside the growing season with the triazine herbicide atrazine present through to October. The most frequently found compounds were two phenoxy acid herbicides, MCPA and dichlorprop.

A number of Swedish lakes which are used as drinking water sources have been investigated for the presence of pesticides (Sandberg and Erlandsson 1990). The result was three positive samples at the 0.1 μgl^{-1} level in raw water of the herbicide bentazone and the phenoxy acid herbicides dichlorprop and MCPA. These substances could not be detected in drinking water. However, in 1990 pesticides were found in 8 of 11 sampled streams in the Göteborg area (City of Göteborg, Environment Protection Board, 1990). The concentration range was 0.1 to 0.3 μgl^{-1} and the detected compounds were the phenoxy acid herbicides MCPA, dichlorprop, 2,4-D, the triazine herbicides terbutylazine, atrazine, simazine, and the herbicide bentazone. More recently a study of 33 sampling points including 10 surface water sources and 23 groundwater sources was carried out in Sweden (Sandberg *et al* 1996). Pesticide residues were found in raw water from one surface water source (on two sampling occasions out of seven) and in three groundwaters (all sampling occasions). The pesticides found were MCPA at the 0.1 μgl^{-1} level in the surface water and atrazine, its degradation product desethylatrazine and 2,6-dichlorobenzamide which is a degradation product of dichlobenil in the groundwater sources. The concentration range was 0.1 to 0.7 μgl^{-1} for the groundwater studied.

More comprehensive surveys have been conducted in Europe and the US which have shown the presence of agricultural pesticides in groundwater. A US survey found 17 different pesticides in the groundwater of 23 states, the most common substance being the carbamate insecticide aldicarb within a concentration range of 1-50 μgl^{-1} (Cohen *et al* 1986). A study in Italy found atrazine in 63% and 15% of private and municipal water reservoirs, respectively (Dahlman 1990).

Legrand *et al* (1991), made a survey in France of 13 sampling points, 11 wells and 2 rivers. They found 38 different pesticides although most were present in concentrations at or below the 0.1 μgl^{-1} level. The triazine herbicides atrazine and simazine were the only compounds detected at levels above 0.1 μgl^{-1} and were found in the rivers Seine and Marne. The phenoxy acid herbicide mecoprop was one of the compounds occasionally found at a concentration between 0.05 and 0.1 μgl^{-1}.

A survey of UK surface and groundwater reported by Foster *et al* (1992) detected the triazine herbicides atrazine and simazine as most commonly occurring. Concentrations were frequently up to 0.6 μgl^{-1}, although maximum concentrations were 9.0 μgl^{-1} for atrazine and 2.8 μgl^{-1} for simazine. Another study also reported the phenoxy acid herbicide mecoprop, the phenylamide herbicide isoproturon and the organochlorine insecticide lindane as frequently found (Foster *et al* 1992). A survey of the river Thames during July 1989 to December 1990 showed two triazine, two phenoxy acid and three phenylamide herbicides present during the entire sampling period. Peak concentrations appeared as a result of application of the pesticides combined with low river

flow or precipitation after a period of dry weather. The study also showed that different pesticides have different seasonal variations depending on which time of the year the compounds were applied. The triazine herbicides atrazine, simazine and the phenylamide herbicide diuron had peak concentrations in the summer and autumn periods whereas the phenylamide herbicides isoproturon, chlortoluron, and the phenoxy acid herbicide mecoprop appeared in the winter and spring periods.

Waite *et al* (1992) studied five pesticides in a small agricultural watershed in Canada. Pesticide residues were found in 47% of 105 groundwater samples and the concentration range was 0.6 to 4.88 μgl^{-1}. The most frequently found pesticide was the phenoxy acid herbicide diclofop, which also had the highest detected concentration. Frank *et al* (1982) studied the Great Lakes basin in Canada. They investigated the sources and transport routes for pesticides into stream or river water and suggested that if the concentration suddenly increases and then declines rather quickly, it is probably a spill event that caused the peak. This may be the direct result of careless procedures before spraying, or cleaning the equipment in the stream water or close to it. Peak concentrations can also appear as a result of heavy rainfall after pesticide application. Losses during spring runoff are often a significant proportion of total yearly loss. Their results showed that during the spraying season, May to June, 82% of the pesticide loss to water was wind-drift from spraying or spills. The remaining 18% was loss during storm runoff events. If the whole year is considered, the loss from spills was 22%, storm runoff 60% and baseflow 18%. Atrazine, simazine and the organochlorine insecticide endosulfan were detected year round. Sediment analyses in the streams showed no contamination of pesticides and the findings during winter time were probably a function of movement through the soil column by internal soil drainage. It was also shown that the pesticides were stable over a long period of time.

Spalding and Snow (1989) studied Shell Creek in Nebraska, USA. They observed low concentrations of pesticides in baseflow during May, when pesticide application was underway in the watershed. The anilide herbicide alachlor and the triazine herbicides atrazine and cyanazine were detected at concentrations of 1.5, 2.9 and 4.4 μgl^{-1}, respectively. The six other pesticides in the study (butylate, disulfoton, the carbamate herbicide EPTC, the acetamide herbicide metolachlor, the triazine herbicide metribuzine, propachlor and the aniline herbicide trifluralin) were not detected at this time. During a spring runoff event four days later, maximum concentration was reached for alachlor, atrazine and cyanazine. The other six pesticides were then detected within a concentration range of 0.1 to 3.0 μgl^{-1}.

Thurman *et al* (1992) found similar storm runoff distributions for atrazine as Spalding and Snow (1989) and Frank *et al* (1982). The major fraction of the pesticide transport occurred during spring runoff events whereas baseflow transported just a small part of the total. Their study also showed that the pesticide loadings transported in the river are a series of pulses from application in spring and during the summer to autumn. The pulses come after a storm event and decrease gradually both in frequency and intensity. Muir and Grift (1987) found the same pattern during May to October as in previous studies; low concentrations and then suddenly a peak together with a runoff event. In one case, they suspected a spillage into the river or spraying close to the river, a category that Frank *et al* (1982) identified as responsible for 82% of the loss of pesticides to rivers and streams during spring.

Atrazine has been studied with special interest because of its frequent appearance in surface and

groundwater. Pionke and Glotfelty (1992) found atrazine in groundwater at high concentrations during the summer and at lower concentrations in the following spring before the next spraying season. Grandet *et al* (1989) have studied atrazine and the metabolite desethylatrazine in groundwater and tried to correlate pesticide concentration with spraying and precipitation, however no direct correlation between atrazine and the degradation product desethylatrazine concentration and precipitation data could be established. They explained the result by suggesting that even if the amount of atrazine and desethylatrazine transported to groundwater increases during rainfall there is a dilution with uncontaminated water and an increase in concentration cannot be seen. The ratio of desethylatrazine/atrazine indicates groundwater contamination as desethylatrazine is more water soluble and transports through soils (Pereira and Hostettler 1993). A ratio of >1 indicates contaminated groundwater, while <0.1-0.4 is typical for surface runoff.

From the literature it can be concluded that detectable amounts of pesticides can be found in rivers and streams during spring when spraying begins. Peak concentration correlates well with runoff events after application and throughout the summer and autumn. Peak concentrations not correlated to runoff events can be regarded as spillage and careless handling of the compounds or equipment. Some pesticides can be found during the non-spraying season, for example triazine compounds. However, the discharge into the aquatic environment is low compared to the amounts applied, in fact only about 0.1 % (Muir and Grift, 1987; Frank *et al* 1982). A number of detailed mass flow/balance studies have demonstrated that the loss of applied atrazine to surface waters is about 1.5% (Schottler *et al* 1994), 1.8% (Ng *et al* 1995) or about 2% (Pereira and Rostad 1990).

It is difficult to compare different investigations because the results depend on when the sampling was carried out; either before/after application or during/between storm events. Other factors are for example the size of the drainage area, soil type and well depth. The pattern of contamination for surface water and groundwater is also different. However, it can generally be stated that atrazine and its metabolite, desethylatrazine pose a problem for groundwater and surface water supplies in Europe (Skark and Zullei-Siebert 1994). The application of soluble herbicides such as the triazines and chlorophenoxy acids in watersheds feeding water supplies causes problems in meeting increasingly stringent European directives.

2.1.5 Pesticide Directives for drinking water

The Commission of the Economic Community (EC) have set acceptable limits, called Maximum Admissible Concentration (MAC), for pesticides in drinking water such that an individual pesticide should not exceed 0.1 μgl^{-1} and total pesticides and low molecular weight organics should not exceed 0.5 μgl^{-1} (Sandberg 1992). The values do not account for different detection limits or toxicity of each pesticide, although they are useful as a general aim. The EC has clearly stated that pesticides have no place in drinking water and the MAC value should therefore be set close to the detection limit (Mandl 1992). In many areas of Europe it is doubtful whether more effective treatment processes alone can sufficiently reduce pesticide concentrations and it will be necessary to implement a management plan which controls the application of pesticides and includes treatment processes. There is no mention in the EC standards concerning analytical methods or water treatment technology, in contrast to the US regulations.

Table 2.4 Comparison of pesticide regulations in different countries.

Pesticide	US[1] Maximum Contamination Level mgl^{-1}	Canadian[2] Maximum Acceptable Level mgl^{-1}	EC[2] Maximum Admissible Level mgl^{-1}	WHO[2] Guideline Value mgl^{-1}
2,4-D	0.07	0.1	NS	0.001
Endrin	0.002	0.0002	NS	NS
Lindane	0.0002	0.004	NS	NS
Methoxychlor	0.04	0.1	NS	0.001
Pesticide	NS	0.1	0.005	NS
Toxaphene	0.005	0.005	NS	NS
2,4,5-TP	0.05	0.01	NS	NS

NS=no standard; [1] Pontius (1995); [2] Sayre (1988).

The United States Environmental Protection Agency (US EPA) has established Maximum Contaminant Level, MCL, for selected pesticides (Pontius 1995). When the US EPA set the contaminant levels, several aspects were taken into account, including occurrence in the environment and health effects caused by exposure to the compound, analytical methods and monitoring, and treatment technologies and costs. The US EPA also recommends Best Available Technology (BAT) for the removal of contaminants at a reasonable cost (Pontius 1995). A comparison of different standards is presented in Table 2.4. The US maximum contaminant level is enforceable whereas the other countries set non-enforceable guidelines.

Canada has quality guidelines for different organic compounds, including pesticides (Table 2.4). There is also a guideline for the total concentration of pesticides, set to 0.1 mgl^{-1} (Sayre 1988). The WHO guidelines for pesticides are based on toxicity tests for each compound. A Tolerable Daily Intake, TDI, is calculated from a No Observed Adverse Effect Level, NOAEL, and the guideline value is 10% of the TDI for an adult (60 kg) assuming an intake of 2 litres of drinking water per day (Sandberg 1992). In the most recent WHO guideline from 1992, 38 pesticides have been given individual guideline values (Sandberg *et al* 1996). Sweden has no set guideline. The drinking water ordinance of 1993 states that drinking water treatment plants have to report findings of pesticides to the National Food Administration (National Food Administration 1993). Certainly, seasonal variations can easily be overlooked, even in sampling programs with quarterly or monthly sampling. The MCL for atrazine of 3 μgl^{-1} in the USA has been considered only a minor health risk for drinking water (Richards *et al* 1995) with only 0.25% of the population affected.

2.1.6 Treatment of pesticides in water treatment plants

There is a significant literature concerning treatment methods to control pesticide residues in drinking water. It can be stated that the conventional treatment unit operations used by many waterworks today do not remove pesticides in general, even if they have some effect on certain compounds. Miltner *et al* (1989) have shown that chemical flocculation, rapid sand filtration, and chlorination do not have much of an effect on trace pesticide concentrations. Aeration is another conventional technique used for the removal of volatile organic contaminants in drinking water and Kruithof *et al* (1993) showed that aeration has no direct effect on the removal of pesticides. Normann *et al* (1987) reported full-scale treatment data with aeration, flocculation and sand filtration. The result was a poor removal, 0% to 33%, of the triazine herbicides atrazine, simazine, propazine, terbutylazine, and the herbicides metolachlor and metazachlor.

Certain pesticides, Miltner *et al* (1989) gave the triazine herbicide metribuzine as an example, are reduced in concentration after chlorination, but with a range of unidentified oxidation products in their place. Another example is that adjustment of pH to over 7 results in hydrolysis of the carbamate insecticide carbofuran. Foster *et al* (1992) have studied the removal of the triazine herbicide atrazine, the phenylamide herbicide isoproturon, the phenoxy acid herbicide mecoprop, and the organochlorine insecticide lindane in full-scale treatment. Pre-chlorination, chemical coagulation and clarification reduced isoproturon from 0.14 μgl^{-1} to 0.02 μgl^{-1} (an 86% reduction) but had no effect for the other pesticides. Rapid sand filtration gave no reduction for the compounds studied. Slow sand filtration reduced mecoprop from 0.08 μgl^{-1} to 0.03 μgl^{-1} (63%) and lindane from 0.15 μgl^{-1} to 0.05 μgl^{-1} (67%) whereas atrazine and isoproturon were unaffected. However, slow sand filtration is an interesting alternative for the more easily biodegradable pesticides, for instance the phenoxy acid herbicides, with removals of 60% to 100% at an influent concentration of 0.1-1.0 μgl^{-1} (Lambert and Graham 1995a).

When a drinking water source has been contaminated with pesticides more efficient treatment methods have to be adopted. The choice of treatment method depends on the pesticide but also on the preferred treatment result. The chosen treatment method can a) remove the pesticide b) degrade the pesticide or c) degrade and remove the pesticide. Adsorption by activated carbon is a treatment method under a), oxidation can be used under b) and ozone, hydrogen peroxide and in some cases chlorination are common oxidation agents. However, the problem with formation of by-products, known and unknown, has to be solved if oxidation processes are to become more widespread for pesticide treatment. In general, oxidation processes only degrade the original contaminant to another and the problem with the health risks associated with drinking water consumption is not necessarily solved. The combination of oxidation and adsorption processes is a further possibility. Ozonation and activated carbon seem to be effective alternatives in the full-scale treatment of pesticide contaminated water (Foster *et al* 1992, Kruithof *et al* 1993).

2.1.6.1 Oxidation of pesticides

A number of oxidants can be used in drinking water treatment, for example, chlorine compounds, ultraviolet (UV) light, hydrogen peroxide and ozone. These oxidants can also be used in combination, for example, UV and hydrogen peroxide, ozone and hydrogen peroxide, ozone and chlorine compounds.

Ozonation as an oxidation technique has been in use since the turn of the century. The treatment aims have been disinfection, taste and odour control, oxidation of iron and manganese, and more recently to enhance the flocculation of suspended solids in surface water (Glaze 1987). Ozone is a strong oxidant and has two different pathways of reacting with organic compounds (Singer 1990). One is a direct reaction of the organic compound with molecular ozone, O_3, which is highly selective. Many organic compounds react in this way, for example activated aromatic compounds, aliphatic alkenes and simple amines. The other pathway is indirect reaction with free radicals which form during the decomposition of ozone. The decomposition of ozone is promoted, for example, by alkaline pH and UV light. The indirect pathway is nonselective and can oxidise compounds that react slowly with molecular ozone, for example aldehydes, ketones, aliphatic acids and less activated aromatic compounds. Under conditions typically found in drinking water treatment, the free radical pathway tends to dominate (Singer 1990).

Treatment with ozone can oxidise organic compounds in water and a number of known and unknown byproducts can form depending on the parent compound. It is a question of whether any organic material really is removed or only degraded when an oxidation treatment method is used. In the literature, some authors use removal, others use degradation to describe the process. In the work of Kruithof *et al* (1993) degradation is used when they reported ozonation experiments with river water and a number of pesticides. Degradation levels between 90 to 100% at 2.2 mgl^{-1} ozone were reported for about half of the pesticides studied while other pesticides were degraded to between 25 and 90%. Atrazine was degraded by 60%.

2.1.6.2 Adsorption of pesticides by activated carbon

Activated carbon has been in use for some time for the removal of organic compounds causing taste and odour problems. Most applications here used the adsorptive capacity of activated carbon, but this makes the technique expensive compared to sand filters due to the need to regenerate the carbon.

Laboratory studies of the adsorption isotherms for pesticides with activated carbon indicate, but do not necessarily predict, how effective a treatment step with activated carbon will be. This is due to the adsorption of high molecular weight substances, such as humic acids, which decrease the carbon adsorption capacity for pesticides and other low molecular weight compounds (Munż *et al* 1990). There are also some difficulties in relating controlled laboratory studies, of the adsorption of high concentrations of pesticides, to real conditions where only trace concentrations of pesticides are present. However, certain mathematical models based on laboratory studies have been found to equate reasonably well with pilot scale studies. The different models are used to predict the effluent concentration profile of a certain compound from a GAC filter as a function of volume processed or time of operation and the profiles are commonly called breakthrough curves. Ideal adsorbed solution theory (IAST) has achieved widespread use in predicting synthetic organic chemical (SOC) breakthrough from GAC filters using single-solute adsorption isotherms as input data (Crittenden *et al* 1987, Sontheimer *et al* 1988, Haist-Gulde *et al* 1991, Qi *et al* 1992). There are also dynamic models that include both film and intraparticle diffusion for the prediction of breakthrough curves, for instance the homogeneous surface diffusion model (Weber and Smith 1987, Pirbazari *et al* 1991). The ability of these models to give reliable predictions of pilot-scale or full-scale GAC filter capacity depends on the laboratory experiments used to obtain

the input data and how well the models describe the interactions during adsorption.

The type of activated carbon used in laboratory experiments also affects the characteristic adsorption isotherms, with the greatest differences between PAC and GAC. The usual practice is to pulverise GAC to PAC to reduce experimental equilibration time. Further, the application of adsorption isotherms will also be affected by differences in batches of the same activated carbon, different technical processes, different properties and concentrations of the pesticides to be removed (Huber *et al* 1989).

Pilot-scale studies using packed columns usually lead to a rapid coverage of the surface by humic substances, however, low molecular weight compounds such as pesticides continue to be effectively adsorbed after the humic substances (Munz *et al* 1990). Improved adsorption can be achieved through the use of "layered upflow carbon adsorption" where the carbon bed depth is successively increased over time by 0.3 m (Munz *et al* 1990).

Full-scale applications of activated carbon are used by most treatment plants along the river Rhine to remove SOC's (Huber *et al* 1989). The presence of pesticides in both ground and surface water is a problem. Effective removal can be achieved through the use of a packed column of GAC. However, where a known one-off contamination is found the batch addition of PAC may be more satisfactory (Miltner *et al* 1989). Wölfel (1989) made a comparison of the same activated carbon used in pilot scale columns and full scale filters. A more effective removal of the herbicide atrazine (0.22 $\mu g l^{-1}$) and desethylatrazine, a degradation product of atrazine, in contaminated groundwater was found in the pilot scale column. This was explained by a longer retention time which may have allowed biological degradation of the compounds. It has been shown that the primary metabolites of a range of s-triazines (such as desethylatrazine for atrazine) are readily treatable by activated carbon (Adams and Watson 1996).

A reduced effect of activated carbon adsorption due to background NOM is now a well established phenomenon, and is usually termed either preloading or competitive adsorption/interaction. A whole range of pesticides have their removal efficiency reduced by preloading (Matsui *et al* 1994, Urano *et al* 1991), this redution is fairly constant and is not affected in small columns by varied or intermittent initial pesticide concentrations. The presence of molecular oxygen increases the adsorption of NOM on the GAC surface (this is typical for polar substances such as phenols and NOM, Warta *et al* 1995) and therefore the capacity for pesticides decreases due to competitive effects (Cerminara *et al* 1995).

The actual mechanism for removal of both SOC's and NOM by activated carbon is an area of active current research, partly because of the emphasis on preventing disinfection by-product formation (Jacangelo *et al* 1995). The adsorption of polar and non-polar organic compounds from solution onto the surface of activated carbon occurs primarily as a result of weak electromagnetic interactions (Lambert and Graham 1995b). The adsorption of humic substances is not irreversible as commonly supposed, although because of the slow desorption of humic substances, displacement by SOC's can generally be ignored (Johannsen *et al* 1994a). However, humic substances have been shown to affect the kinetics of SOC adsorption by reducing external and internal mass transfer (Johannsen *et al* 1994b). Lambert and Graham (1995b) have suggested that the larger MW fractions are adsorbed on the basis of changes in UV/VIS absorption. This is misleading as humic UV/VIS absorption increases with MW.

The most likely explanation is as follows. Adsorption potential increases with MW of humic substance due to increasing hydrophobicity and more binding sites per molecule. However, humic substance of a smaller MW penetrates deeper into the GAC micropores where there is a greater area available for adsorption. This explains why Johannsen *et al* (1993) observed that the adsorption of humic substances to GAC increases with a decrease in molecular size. Once adsorbed, NOM decreases adsorption capacity by decreasing available surface area and increasing the negative charge on the GAC surface (Newcombe *et al* 1993, Newcombe 1994, Morris and Newcombe 1993).

2.1.6.3 Biological degradation of pesticides on activated carbon

Biological growth on activated carbon is usually regarded as a problem which is avoided by short contact times and frequent backwashing. However, by allowing and even enhancing bacterial growth on activated carbon through longer contact times it may be possible to stimulate the natural degradation of pesticides. Biologically activated carbon has been shown to be effective for SOC's such as chlorinated phenols (Speitel *et al* 1989). Desorption due to varying incoming concentrations may not be a problem in the biological system as adsorbed substances may be degraded. In fact, the biological system should cope well with varying concentrations of pesticides as during low concentration exposure the adsorption surface can be regenerated by biological degradation to allow direct adsorption during high concentration exposure.

Laboratory and pilot tests usually employ either a one column system with bacteria in a part or in all of the column, or a two column system in series with one column free from bacteria to adsorb degradation products (Gmünder *et al* 1989). In addition the latter prevents bacterial contamination of treated water (Bouwer and Crowe, 1988), although a further disinfection step is usually considered necessary. The organisms used in laboratory studies are usually those found in the incoming raw water and consequently a pre-disinfection step is of course avoided. The bacterial culture that grows on activated carbon is fast-growing and is adapted to colonising fresh surfaces (Bouwer and Crowe, 1988). One concern is an increased number of microorganisms in drinking water after treatment with biologically activated carbon filters. LeChevallier and McFeters (1990) reported in a comprehensive literature review that microorganisms are released from GAC filters through attachment to carbon particles that leave the filter and enter drinking water. However, the significance of the released microorganisms is unclear, especially the presence of coliforms and pathogens in the biofilm on the activated carbon particles.

Full scale tests on biologically activated carbon filters have been carried out at the Mülheim waterworks in Germany (Sontheimer 1978, Sontheimer *et al* 1978). Biological degradation of organic material decreased after pre-chlorination, but increased after pre-ozonation. The latter is due to partial degradation of organic substances by ozonation which increases the available substrate for the bacteria.

The effectiveness of biologically activated carbon in removing pesticides has not been widely tested. However, Selim and Wang (1993) have studied the breakdown of atrazine in a laboratory scale biologically activated carbon column. The result showed that 99% of the applied atrazine was degraded in the column. Complete mineralisation to CO_2 of atrazine and the atrazine degradation products, desethylatrazine, deisopropylatrazine and hydroxyatrazine, occurred.

It is also not known whether the pesticide concentrations found in contaminated raw water can have a toxic effect on the colonised bacteria. The sensitivity of the light-emitting bacterium *Photobacterium phosphoreum* (Microtox) and mixed algae/bacteria cultures to pesticides (McFeters *et al* 1983) are shown in Table 2.5. Although the Microtox bacterium is not the same as those found in biological activated carbon filters, it does give an indication of the magnitude of pesticide concentration required to inhibit 50% of a population of bacteria. Cultures containing algae are effectively destroyed by low concentrations of chlorophyll acting herbicides. However, Microtox bacteria survive at concentrations (mgl^{-1}) well above those found even in contaminated raw waters (typically μgl^{-1} - lower mgl^{-1}). Although certain sensitive bacteria may be affected by pesticides, it would seem unlikely that pesticides will affect the bacteria community as a whole and therefore the general performance of biological filters.

Table 2.5 Toxicity of herbicides (H) and insecticides (I) to algae/bacteria and Photobacterium phosphoreum (Microtox) populations.

	EC_{50}, mgl^{-1}	
	Algae/bacteria	Microtox
Diuron (H)	0.04	16
Simazine (H)	1.1	240
Malathion (I)	18	60
2,4-D (H)	250	62
Bromacil (H)	nt	7
Heptachlor-epoxide (I)	nt	25

nt = not tested

An alternative approach to using the natural bacterial community is to isolate specific strains of bacteria from surface and treated waters that show an effective biodegradation of pesticides (Feakin *et al* 1994a). These bacteria can then be innoculated onto GAC filters; effective atrazine removal was achieved after 40 days in GAC pilot filters (Feakin *et al* 1994b).

2.1.6.4 Membrane filtration

Membrane filtration is a relatively new development in water treatment. With a pore size of approximately 10 nm ultrafiltration does not remove pesticides (Duguet *et al* 1993). Low pressure nanofiltration, with a pore size of 0.001 µm removes 66-98% of triazines and has been shown to effectively remove NOM in water treatment (Jacangelo *et al* 1995). In order to meet European Directives, nanofiltration would need to be combined with activated carbon adsorption (Duguet *et al* 1993, Hopman *et al* 1996).

2.1.7 Conclusions

The presence of pesticides in the aquatic environment represents a potential threat to water quality and human health. Relatively soluble herbicides, such as the chlorphenoxy acids and triazines, applied in agriculture can reach drinking water sources. These herbicides show marked seasonal variations in concentration and have a longer residence time in groundwater and surface water than was previously believed. Atrazine and its metabolite, desethylatrazine, are a particular concern in many countries. Conventional treatment technologies, such as flocculation/sedimentation, sand filtration and chlorination are ineffective in the control of pesticides. Potential control has focused on technologies that promote biodegradation (slow sand filtration), destruction (ozonation) or adsorption (granular activated carbon). Granular activated carbon has proved the most effective and reliable barrier to the sporadic, seasonal variations of pesticides with different chemical properties. It has now been established that natural organic matter hinders pesticide adsorption through a phenomenon usually termed preloading. Research is therefore now focusing on the identification of the competitive organic fraction, with a view to minimising the concentration of this fraction or preventing preloading.

2.1.8 References

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2.2 Analytical Methods

2.2.1 Introduction

This chapter describes the development of methods for the enrichment and analysis of triazine and phenoxy acid herbicides. Solid-phase extraction (SPE) and high-performance liquid chromatography (HPLC) were used. The triazine compounds tested were atrazine and cyanazine, the phenoxy acid compounds were dichlorprop, MCPA and mecoprop. The names, chemical structures, pK_a values and molecular weights for the studied herbicides are presented in Table 2.6.

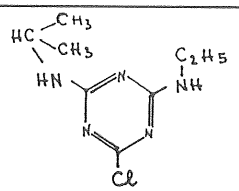
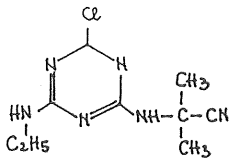
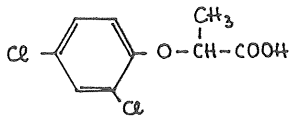
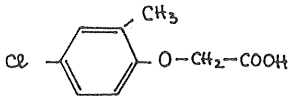
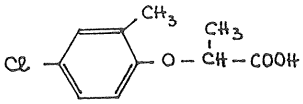
2.2.2 Solid-phase extraction

Solid-phase extraction (SPE) is a technique for the extraction of organic and inorganic solutes from a liquid matrix. After elution from the solid phase, specific compounds can be analysed, for example by chromatographic techniques. It is also possible to separate analytes from a background matrix. SPE avoids many of the disadvantages of liquid-liquid extraction, such as the use of large volumes of solvents, and has been shown to be effective for a wide range of environmental organic pollutants (Barcelo *et al* 1993). One of the goals of this work was to develop a method to analyse pesticides in natural waters by HPLC with SPE as an efficient enrichment step, while at the same time decreasing the concentration of natural organic matter (NOM). The advantage of SPE over the more traditional liquid-liquid extraction is the possibility of extracting large sample volumes both in the laboratory and in the field. This is particularly important for contaminants at low concentrations which require large volumes to achieve improved detection limits.

SPE is carried out using a small column, sometimes also called a cartridge, which is filled with the packing material of choice. A schematic diagram of a SPE column is shown in Figure 2.1. In this work octadecyl bonded (C_{18}) silica packing material was used as recommended by the supplier (Varian). A vacuum manifold or a syringe can be used to enable passage of the water sample and to extract solvents through the column. The column material retains the organic compounds contained in the sample. An organic solvent is used for elution of the organic compounds bound to the solid surface and the eluate can then be analysed. When spiked surface water was used, the NOM was adsorbed to the SPE material and coeluted together with the

pesticides. The HPLC analysis suffered from a large background interference and it became clear that NOM should be eluted from the SPE column before the pesticides were eluted. It was decided to select a washing solution that could elute the NOM and leave the pesticides on the SPE material before final analyte elution.

Table 2.6 Name, chemical structure, pK_a value and molecular weight for the herbicides.

Herbicide	Chemical structure	pK_a	Molecular weight[b]
Triazine			
Atrazine (4-ethylamino-6-chloro-2-isopropylamino-1,3,5-triazine)		1.68[a]	215.7
Cyanazine (4-ethylamino-2-(1-cyano-1-methy-lethylamino)-6-chloro-1,3,5-triazine)			240.7
Phenoxy acid			
Dichlorprop (2-(2,4-dichlorophenoxy)-propanoic acid)		2.86[c]	235.1
MCPA (4-chloro-2-methyl-phenoxy acetic acid)		3.05[d] 3.62[e]	200.6
Mecoprop ((±)-2-(4-chloro-2-methylphenoxy)-propanoic acid)			214.6

[a] Base protonation constant. Pacakova *et al* (1988)
[b] Quentin *et al* (1987)
[c] Jönsson *et al* (1958)
[d] Burström *et al* (1956)
[e] Jönsson *et al* (1952)

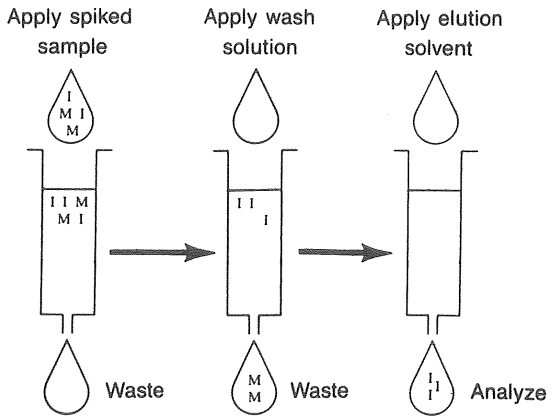


Figure 2.1 Schematic diagram of a SPE column from the Varian Instruction Manual.

2.2.2.1 *Previous efforts to remove background interference*

Hoke *et al* (1986) have analysed the phenoxy acid herbicides 2,4-D, 2,4,5-T and silvex in reagent water and surface water using SPE columns with C_{18} bonded silica. The phenoxy acids were eluted with two 1 ml portions of methanol and diluted with water to 5 ml before HPLC analysis. No attempt was made to wash the column to provide a lower content of NOM in the eluate. The recoveries after elution were much lower for natural waters than for reagent water. Hoke *et al* (1986) interpreted that result as indicating that the phenoxy acids were tightly bound to trace organic material. They made several attempts to improve the recovery, including the use of two SPE columns in series, filtering the water before spiking and addition of sodium chloride, with no positive results. Geerdink *et al* (1989) have used SPE columns with polymeric material, a macroporous polystyrene-divinylbenzene copolymer, for enrichment of the phenoxy acids MCPA, 2,4-D, MCPP, 2,4-DP and 2,4,5-T from samples of tap water and surface water. They used a washing step before the application of the samples with pesticides but this was designed to clean the SPE column and not to remove NOM. The washing solvent was acetonitrile:water (30%:70%) at pH 3. Wells and Michael (1987) have developed a method for separation of the two herbicides picloram and 2,4-D in distilled water and surface water using SPE columns with serial elution of the two substances. Coelution of the two compounds into one eluate would also include contaminants from surface water. Due to the different characteristics of picloram and 2,4-D, there is no need for a separate washing step to minimise dissolved organic material.

Clearly, the problem with NOM in HPLC analysis has not been solved. In this study, several washing solutions were tested to minimise the interference caused by NOM.

2.2.2.2 *Screening to find a washing solution*

The naturally occurring NOM in a lake water (Delsjön) was used to find a solvent that could preferentially elute the NOM but was weak enough to leave the pesticides on the SPE material.

Lake water was passed through a SPE column and then the column was eluted with different elution solvents. The solvents were phosphate buffer at pH 3.0, dilutions of sodium hydroxide (NaOH), and mixed solutions of acetonitrile (CH_3CN), water (H_2O) and methanol (CH_3OH). Serial elution was employed, with methanol used as the last elution solvent to examine the effect of the previous elutions on the UV absorbance value of the methanol eluate. The eluates from five SPE columns were analysed in a UV-spectrophotometer at 254 nm, the wavelength that is typically used for the qualitative measurement of NOM content. NOM can have different UV-absorbance characteristics in different solvents but in this study it was assumed that a high measured value in absorbance units represents a high NOM content in the eluate. The results of the UV analysis are summarised in Table 2.7.

Table 2.7 UV measurement of different eluates.

Elution solvent	Eluate abs_{254}, cm^{-1}				
	SPE columns[a]				
	1	2	3	4	5
Phosphate buffer, pH 3.0	0.153	-	-	-	-
0.1 M HCl	0.025	-	-	-	-
0.1 M NaOH	1.574	1.317	-	-	-
0.01 M NaOH	-	-	0.548	-	-
H_2O:CH_3CN:CH_3OH, 50:38:12%	-	-	-	2.376	-
H_2O:CH_3CN, 55:45%	0.809	-	-	-	-
CH_3CN	-	-	-	-	1.966
MeOH	0.399	0.986	0.949	0.183	0.850

[a] Five Bond-Elute SPE columns

The eluates with high UV-absorbance value were from elution with 0.1 M NaOH, H_2O:CH_3CN:CH_3OH, 50%:38%:12%, H_2O:CH_3CN, 55%:45%, and CH_3CN. They were then tested as washing solutions before elution of the herbicides. Lake water samples were spiked with the herbicides, extracted through SPE, the SPE columns were eluted with the washing solutions and final elution of the herbicides was with methanol. The results from the triazine samples are shown in Table 2.8.

Table 2.8 Test of washing solutions for triazine samples. The arithmetic mean of the recovery is in parentheses.

H_2O	CH_3CN	CH_3OH	% Recovery	
%	%	%	Cyanazine	Atrazine
50	38	12	95.3	102.9
			95.3 (95.3)	96.4 (99.7)
25	75		23.3	57.9
			24.5 (23.9)	57.9 (57.9)
75	25		93.1	99.6
			94.2 (93.6)	101.6 (100.6)

Washing with H_2O:CH_3CN, 25%:75% gave low recovery, especially for cyanazine, whereas the other two gave similar results. Washing with the solution containing methanol seemed to remove NOM better than the solution without methanol because the frontal peak in the chromatogram was smaller and with a improved baseline. The decision was to use the solution of H_2O:CH_3CN:CH_3OH, 50%:38%:12% as washing solution for the triazine enrichment procedure. For phenoxy acid samples 0.1 M NaOH, H_2O:CH_3CN:CH_3OH, 50%:38%:12% and H_2O:CH_3CN, 55%:45% were tested as washing solutions. The results are shown in Table 2.9. The recovery was highest for H_2O:CH_3CN, 55%:45% and was therefore chosen as washing solution for phenoxy acid samples.

Table 2.9 Test of washing solution for phenoxy acid samples. The arithmetic mean of the recovery is in parentheses.

	% Recovery		
Washing solution	MCPA	Dichlorprop	Mecoprop
0.1 M NaOH	58.7	80.7	85.1
	60.1 (59.4)	79.8 (80.3)	85.1 (85.1)
H_2O:CH_3CN:CH_3OH,	41.7	58.2	56.8
50%:38%:12%	53.0 (47.4)	56.8 (57.5)	65.1 (61.0)
H_2O:CH_3CN, 55%:45%	67.8	88.0	87.0
	83.4 (75.6)	89.1 (88.6)	87.1 (87.1)

The volume of the washing solution is also important for recovery. Table 2.10 summarises results from tests with different volumes of the washing solution, which is a non-optimal solution composed of water and acetonitrile, 55%:45%. Ultrapure water and lake water were spiked with

cyanazine and atrazine. Washing with 1.5 ml water:acetonitrile (55%:45%) eluted almost all cyanazine but atrazine was still adsorbed on the SPE column and gave a reasonable recovery. Tests with 0.5 ml washing solution increased the recovery for both substances when ultrapure water was used. However, tests with spiked lake water showed that 0.5 ml was not enough to remove the NOM from the SPE column. It was found that 0.7 ml of washing solution was the smallest volume that could elute the NOM without significant losses of cyanazine and atrazine. The same volume of washing solution was also used for samples containing phenoxy acid herbicides.

Table 2.10 The influence of washing solution volume on recovery of cyanazine and atrazine.

Volume ml	% Recovery	
	Cyanazine	Atrazine
1.5	trace[a]	83.0[a]
0.7	80.0[b]	87.0[b]
0.5	98.0[a]	101.5[a]

[a] spiked ultrapure water
[b] spiked lake water

2.2.2.3 *The pH dependence of the SPE method*

It is important to carry out the SPE enrichment at a suitable pH to get the highest recovery. Therefore the pH dependence of the SPE was tested in lake water spiked with phenoxy acids and triazines. For the phenoxy acids, a pH range of 2 to 5 was tested and the best recovery was obtained at pH 2 (Table 2.11). The triazines was tested over a pH range of 2 to 9 and the best recovery was obtained at pH 7.5 (Table 2.12).

Table 2.11 pH dependence for the recovery of phenoxy acids from a SPE. Standard deviations (SD) with number of samples (n) are also reported.

pH	MCPA % recovery	SD	n	Dichlorprop % recovery	SD	n	Mecoprop % recovery	SD	n
2.2	99.7	11.7	6	96.1	10.1	6	96.3	2.4	6
3.0	103.6	11.8	4	105.9	11.7	3	118.1	17.2	5
4.0	79.0	8.5	6	80.5	6.7	6	92.0	9.1	6
5.0	12.4	0	2	43.2	5.7	4	65.6	4.2	4

Table 2.12 pH dependence for the recovery of triazines from a SPE. Standard deviations (SD) and number of samples (n) are also reported.

pH	Cyanazine % recovery	SD	n	Atrazine % recovery	SD	n
2.2	46.8	17.5	6	84.2	1.9	6
5.0	35.5	5.3	4	78.6	0.6	4
7.5	51.2	9.3	6	95.7	2.8	6
9.0	44.4	8.2	4	92.0	2.2	4

2.2.2.4 Final selected conditions

Conditioning of the SPE columns included elution with 2 ml of methanol and 2 ml of ultrapure water before sample extraction. Sample preparation to retain column condition involved addition of 1 ml of methanol to each 50-100 ml of sample for both phenoxy acid and triazine samples. The most suitable extraction pH for phenoxy acids was pH 2, whereas a neutral pH value was satisfactory for extraction of triazines. The washing solution for phenoxy acids was 0.7 ml of water and acetonitrile, 55%:45%, and 0.7 ml of water, acetonitrile and methanol, 50%:38%:12%, for triazine samples.

2.2.3 High-Performance Liquid Chromatography

2.2.3.1 Selection of HPLC conditions for phenoxy acids

The intent was to develop a reversed-phase HPLC method with an octadecyl bonded silica column and an acidic mobile phase. Hoke et al (1986) used an octyl (C_8) bonded silica column, a mobile phase of methanol and 1% acetic acid (68%:32%) and UV-detection at 280 nm. DiCorcia *et al* (1989) used an octadecyl (C_{18}) bonded silica column together with a mobile phase of methanol and 0.08% trifluoroacetic acid and UV-detection at 230 nm. The composition of the mobile phase affects the selection of the detection wavelength. Phenoxy acids have two UV absorption maxima, at 230 nm and 280 nm, as shown in the absorption curve in Figure 2.2. Detection at 280 nm gives a chromatographic peak that is low and broad, as previously reported in the literature (Hoke *et al* 1986), while 230 nm gives a sharp peak. 235 nm was selected as the detection wavelength as it gives a sharp chromatographic peak. Hoke *et al* (1986) found a baseline with a high signal to noise ratio at 235 nm and a low sensitivity at 280 nm; similar results were found in this study as indicated by the chromatograms in Figure 2. 3. An explanation for this result is given by DiCorcia *et al* (1989). They claim that acetic acid in the mobile phase gives problems with the baseline when 230 nm is used as the detection wavelength and in their method they replaced acetic acid with trifluoroacetic acid. However, in this work, tests showed that acetic acid could be replaced with 0.01 M phosphate buffer at pH 3. The baseline at 235 nm improved and a satisfactory separation was found between the phenoxy acids (Figure 2.4).

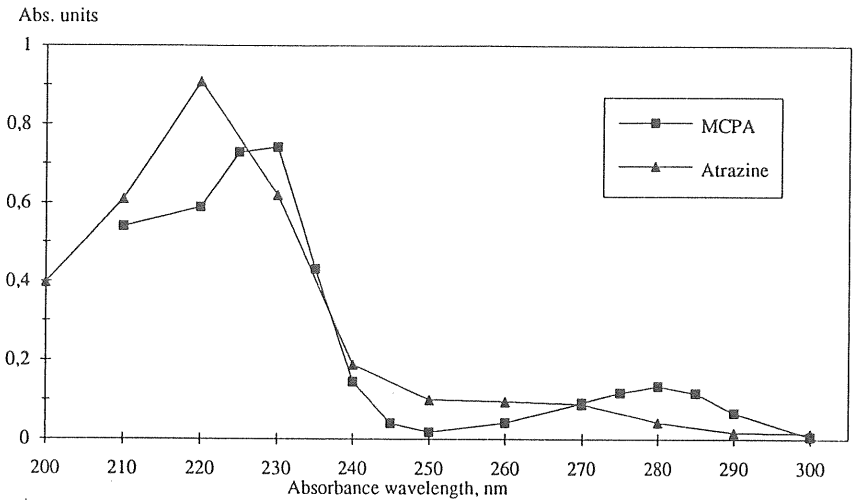
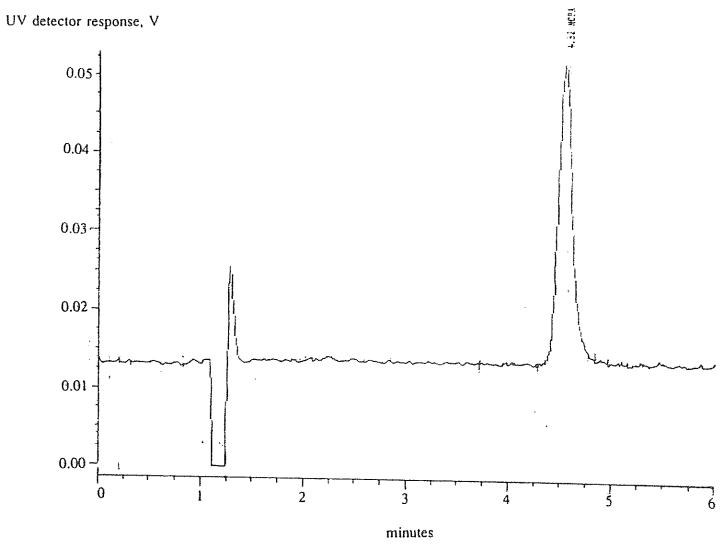
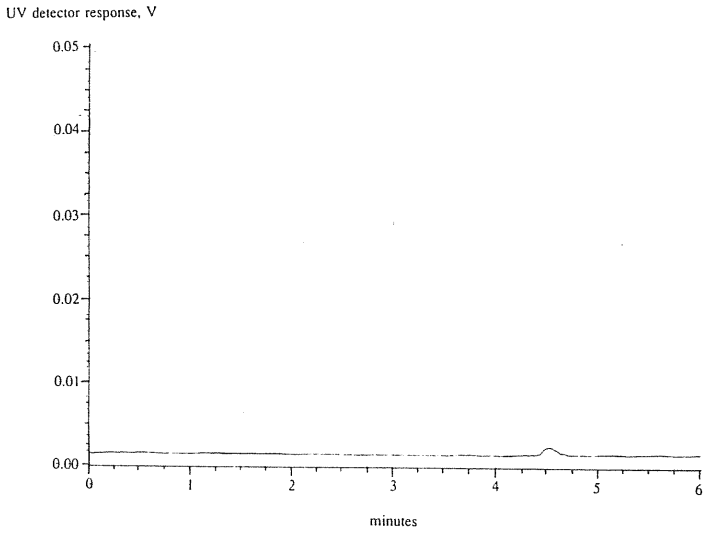


Figure 2.2 Measurement of UV absorbance of MCPA and atrazine.



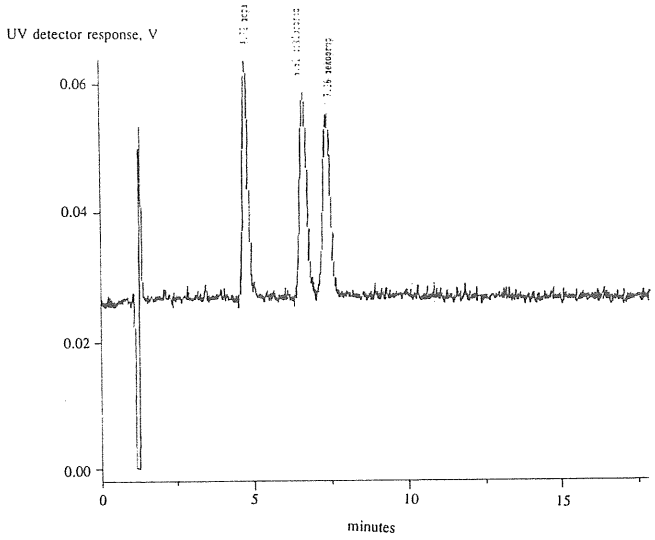
a)



b)

Figure 2.3 Chromatograms of MCPA with a) 235 nm and b) 280 nm as detection wavelength.

a)



b)

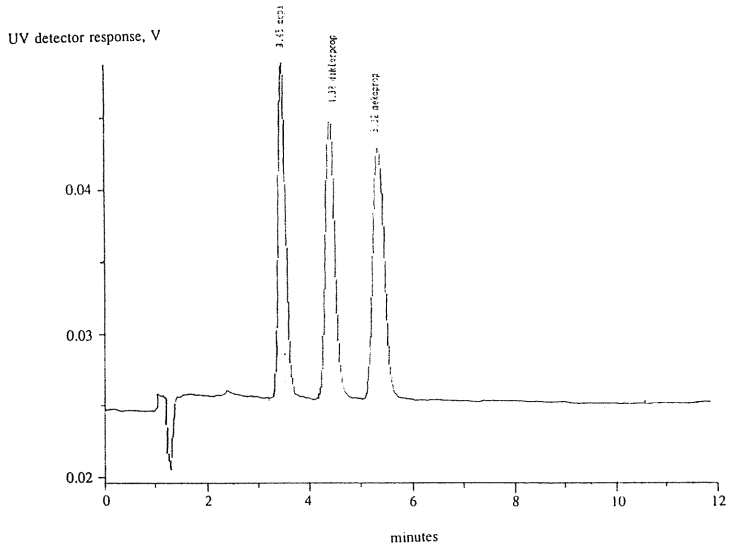


Figure 2.4 Comparison of mobile phase composition, 235 nm as detection wavelength.
a) methanol: 1% acetic acid 60%:40%
b) methanol: pH 3 phosphate buffer 60%:40%

The variation in retention time for MCPA for different mobile phase compositions and two types of C_{18} bonded silica columns is shown in Table 2.13. The system that had the shortest retention time for MCPA was chosen.

Table 2.13 Retention time for MCPA in different HPLC systems. C_{18} column, 1 ml min^{-1} flow rate, 60%:40% composition of mobile phase.

Mobile phase	Column	Retention time (min.)
MeOH:CH_3COOH, 1%	NovaPak	4.5
MeOH:CH_3COOH, 1%	Resolve	5.0
MeOH:phosphate buffer, pH 3	Resolve	3.5

Tests were also carried out with a more concentrated phosphate buffer, 0.02 M at pH 3. This resulted in shorter retention times, as shown in Table 2.14. The mobile phase should have a salt content as low as possible because precipitation of buffer salt can damage the column and cause blockage in the connections, consequently a buffer strength of 0.01 M was chosen.

Table 2.14 Retention time for the phenoxy acids MCPA, dichlorprop and mecoprop for two buffer concentrations at pH 3.0.

	Retention time (min)	
	Phosphate Buffer concentration	
	0.01 M	0.02 M
MCPA	4.1	3.7
Dichlorprop	5.3	4.8
Mecoprop	6.5	5.9

The pK_a values of the phenoxy acids MCPA and dichlorprop are close to 3, as shown in Table 2.6. When the mobile phase has the same pH as the pK_a the mixture of protonated and unprotonated species can make the peak broader and decrease the separation between compounds compared to a mobile phase with lower or higher pH. The lower limit of pH of the mobile phase is set to 2 by the octadecyl silica material in the column. The only alternative in this system, to test if the pH affects the chromatographic performance, is to raise the pH. Therefore a mobile phase with methanol and 0.01 M phosphate buffer at pH 4.5, was tested. The result was that the retention times for the three compounds became shorter and the separation decreased. It was decided to continue to use a pH value of 3.

2.2.3.2 *Selected final method for phenoxy acids*

After the preliminary investigations and on the basis of reported literature, an octadecyl silica column, Resolve (Waters), together with a mobile phase consisting of methanol and phosphate buffer with a concentration of 0.01 M at pH 3, 60%:40% was chosen. The detection wavelength was set to 235 nm and the flow rate to 1 ml min^{-1}.

2.2.3.3 *Selection of HPLC conditions for triazines*

Triazine herbicides are weak bases which protonate and form cations at low pH values and are unprotonated at pH values of 6 to 7 (Loch 1991, Pacakova *et al* 1988). Battista *et al* (1989) suggested a reversed phase system with a mobile phase of acetonitrile and phosphate buffer (38%:62%, vol:vol) at pH 6.7 and 0.01 M together with an octadecyl bonded silica column and UV-detection wavelength of 220 nm. Results from tests of the method of Battista *et al* (1989) are shown in Table 2.15. Different proportions of acetonitrile and phosphate buffer at pH 6.7 and two different flow rates were tested.

Table 2.15 Retention time of atrazine.

Mobile phase CH_3CN:Buffer pH 6.7 %	Flow rate ml min^{-1}	Retention time min
30:70	1.0	8.4
38:62	1.0	4.8
38:62	2.0	2.5

The method worked well for a range of reversed phase columns (Table 2.16) although NovaPak was chosen on the basis of convenience. Further testing showed that 0.01 M phosphate buffer at pH 6.7 could be replaced by ultrapure water with a pH of 6 to 6.5, thereby simplifying the method. It was found that a NovaPak C_{18} column successfully separated atrazine from cyanazine. The samples were 1.0 mg l^{-1} standard solutions of atrazine and mixed atrazine/cyanazine in ultrapure water.

Table 2.16 Test with different columns and mobile phase compositions. Flow rate 1 ml min^{-1}

Column	Mobile phase %	Retention time (min)	
		Atrazine	Cyanazine
NovaPak C_{18} 150*3.9 mm	CH_3CN:buffer pH 6.7 38:62	4.8	na
NovaPak C_{18} 150*3.9 mm	CH_3CN:H_2O 45:55	3.7	2.6
NovaPak C_{18} 300*3.9 mm	CH_3CN:H_2O 60:40	4.0	na
Supelcosil LC-PAH 250*4.9 mm	MeOH:H_2O 60:40	6.0	na
µBondaPak C_{18} 150*3.9 mm	CH_3CN:H_2O 60:40	2.9	na

na = not analysed

2.2.3.4 *Selected final method for triazines*

The octadecyl silica column, NovaPak (Waters), was chosen together with a mobile phase composition of acetonitrile and water, 45%:55% by volume. The detection wavelength was set to 220 nm and the flow rate to 1 ml min^{-1}.

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PART 3 RESEARCH

3.1 Pesticide interaction with activated carbon in the presence of dissolved organic material

This article reports on the analytical methods developed for triazine and phenoxy acid herbicides together with adsorption studies of the herbicides atrazine and MCPA. Freundlich adsorption isotherms show interference from dissolved organic material in pesticide adsorption for untreated and treated water from the Lackarebäck drinking water treatment plant.

Figures 1 and 2 show adsorption isotherms of atrazine and MCPS with natural logarithm, ln, on the axes. In the figures following the article the axes have been corrected to logarithmic scales.

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Pesticide interaction with activated carbon in the presence of dissolved organic material

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ABSTRACT

Une méthode a été développée pour l'analyse des pesticides atrazine, cyanazine, dichlorprop, MCPA, mecoprop et bentazone, par extraction de la phase solide (SPE) suivie d'une chromotographie du liquide. L'interférence de matériaux organiques dissous (DOM) lors de l'analyse finale a pu être évitée grâce à la sélection d'un éluent approprié dans la première partie du procédé (SPE). La méthode proposée a été utilisée pour l'analyse en laboratoire de l'adsorption de pesticides par du carbone activé (AC). L'adsorption de l'atrazine par le AC a été étudiée dans de l'eau purifiée ainsi que dans de l'eau provenant d'un lac, et comparée à de l'eau de lac après traitement à grande échelle par floculation de l'aluminium et AC, ainsi qu'après un essai-pilote de traitement à l'ozone. Il a été trouvé que DOM peut compétitionner avec l'atrazine pour les sites actifs du AC, même après floculation de l'aluminium et ozonation. DOM a le même effet sur l'adsorption de MCPA par AC dans de l'eau de lac non-traitée. Par conséquent, l'adsorption compétitive par DOM réduit la vie effective de la couche active et les prédictions du sueil de percée obtenues pour le AC à l'aide des données d'adsorption isotherme.

INTRODUCTION

There is an increasing concern over the possibility of pesticides entering the aquatic environment and contaminating drinking water at source. It is therefore appropriate to address the effectiveness of conventional drinking water treatment for pesticide removal.

Although agricultural application to crops is generally regarded as the major contribution of pesticides to source waters it is also recognised that in urban areas household and highway usage may also be significant. Certain groups of pesticides are more persistent in the aquatic environment including the s-triazines, phenoxyacids and bentazone. s-Triazines have been measured in French ground and surface waters (Legrand, 1991) and it has been estimated that 5-10 % of German water supplies have a pesticide problem (Opie, 1992). The low concentrations of pesticides can be determined by preliminary concentration/separation using solid-phase extraction (SPE) followed by high performance liquid chromatography (HPLC), (Barcelo, 1988; Junk, 1988).

Treatment for pesticides might include the use of activated carbon (AC). AC has been shown to successfully remove natural concentrations of s-triazines when incorporated in drinking water treatment (Marcomini, 1991). The bed-life and the breakthrough curves for individual pesticides are revealed if accurate adsorption isotherms can be obtained. Isotherm accuracy depends on a thorough consideration of parameters affecting adsorption including pH, ionic strength, dissolved organic material (DOM) and type of AC (Crittenden, 1987). Granular activated carbon (GAC) requires long equilibration times and therefore pulverised GAC is usually recommended for adsorption isotherms (Randtke, 1983), although equilibrium can still take up to three days.

The presence of DOM in water is known to affect the adsorption of pesticides to AC (Pirbazari,1992), although it is uncertain whether the reduction in capacity is due to complexation or competitive adsorption. Complexation involves the formation of DOM-pesticide complexes which may or may not be adsorbed by the AC surface. Competitive adsorption occurs between the pesticide and a physically or chemically similar fraction of the DOM for an active site on the AC.

Two groups of herbicides were regarded as interesting, phenoxy acids and s-triazines. One of the phenoxy acids, MCPA, is the most widely used herbicide in Sweden. Atrazine is forbidden in Sweden but residues are still found in the aquatic environment. Bentazone has been found in groundwater in the south of Sweden (Sandberg, 1990).

In this investigation a HPLC method for the analysis of selected pesticides in raw water and drinking water is improved. Laboratory bench-scale experiments are carried out to investigate the interaction of atrazine and MCPA with AC in the presence of DOM in lake water. Results are compared with the same lake water after full-scale treatment by aluminium flocculation and AC filtration and after pilot-scale treatment with ozone.

EXPERIMENTAL

Due to the different character of the compounds two different HPLC separation methods and enrichment procedures were developed. The phenoxy acids require a mobile phase at pH 3, whereas the s-triazines separate at neutral pH. The optimum absorbance wavelength is also different, phenoxy acids absorb at 235 nm and s-triazine at 220 nm.

Solid-Phase Extraction

The cartridge used for SPE was Bond Elute (Analytichem, Varian), octadecyl bonded silica, 500 mg with 3 ml cartridge volume and 75 ml reservoirs. The SPE column was placed in a small filter bottle attached to a filter pump and the samples were extracted at a flow rate of ~5 $mlmin^{-1}$. The SPE column was preconditioned with 3-6 ml of methanol and 3-6 ml ultrapure water. Spiked samples in ultrapure water or lake water were prepared in 100 ml or 1000 ml volumetric flasks from the 10 mgl^{-1} working standard, with the addition of 1 ml of methanol to retain the condition of the SPE columns. The sample was applied, followed by a few ml of ultrapure water to wash the volumetric flask and 0.7 ml of wash solution (see table 2). Finally the analytes were eluted with 1.5 ml methanol into a 2 ml volumetric flask. After dilution with ultrapure water or phosphate buffer to the mark, 100 µl was injected into the HPLC.

A control sample, representing 100% recovery was prepared in a 2 ml volumetric flask with 1 ml of methanol and a known pesticide standard and diluted with reagent water or phosphate buffer to the mark. 100 µl of this solution was injected into the HPLC.

HPLC Separation and Analysis

The HPLC-system was a Waters system, (Millipore,USA) including a gradient pump 600, multichannel UV-detector 490 and autoinjector satellite-WISP 700. The analytical columns used were Waters Nova Pak and Waters Resolve octadecyl bonded silica (C_{18}), 150*3.9 mm, 5 µm particle size. Precolumns were used. The s-triazines were separated on the Nova Pak C_{18} column with acetonitrile:water (45%:55%) as mobile phase. The detection wavelength was 220 nm. For the phenoxy acids, the Resolve C_{18} column was used with methanol:0.01 M phosphate buffer, pH 3.0 (60%:40%) as mobile phase. The detection wavelength was 235 nm.

In both methods the flow rate was 1.0 $mlmin^{-1}$ and the sample volume was 100 µl. Calibration curves were obtained by means of three standards.

Reagents and Standards

Organic solvents, methanol and acetonitrile, were of HPLC-grade from Merck and ultrapure water was obtained from a Barnstead NanoPure system. The 0.01 M phosphate buffer pH 3.0, was made from NaH_2PO_4:H_2O, p.a grade and H_3PO_4 p.a grade from Merck. The buffer was filtered through a Durapore 0.45 µm filter (Millipore) before use.

The pesticides tested were atrazine, cyanazine, dichlorprop, MCPA, mecoprop and bentazone. Atrazine and MCPA were Certified Reference Material from the Laboratory of the Government Chemist, UK. The other pesticides were obtained from Dr Ehrenstorfer, Augsburg, Germany. The purity of the substances was in the range of 99.3% to 99.9%.

A stock solution of each compound containing 100 mgl^{-1} dissolved in methanol (phenoxy acids) or acetonitrile (s-triazines) was prepared. Dilutions were made with ultrapure water to produce 10 mgl^{-1} working standards of phenoxy acids and s-triazines.

Sampling

Lake water was sampled from Delsjön, which is an important source for the Göteborg drinking water treatment plant at Lackarebäck. Samples were taken after full scale treatment with alumninium flocculation, AC filtration and pilot scale ozone treatment, with and without aluminium flocculation and sand filtration. Water characteristics for the samples are presented in Table 1.

TABLE 1. Water characteristics

	pH	DOM, mgl^{-1}
Lake water	7.5	4.0
Full scale treatment		
Aluminium flocculation	6.4	1.1
AC filtration	6.7	1.1
Pilot scale treatment		
Ozone	7.2	3.6
Ozone,aluminium flocculation, sand filtration	6.6	1.0

Description of the Adsorption Studies

The adsorption studies were carried out in glass beakers (1 litre) stirred with a paddle. Each series of experiments contained 14 beakers. The samples were buffered with 0.01 M KH_2PO_4 and 0.01 M NaOH, pH 7. Lake water was initially filtered through glassfibre filters GF/C,

but when bacterial growth was observed in the experiments, 0.45 µm cellulose acetate filters were used instead. The AC was Filtrasorb 300 (Chemviron) that was pulverised and sieved. The fraction that passed 63 µm was dried in 105°C for 24 hours and stored in a desiccator until used in the experiments. The AC was then weighed and suspended in ultrapure water (0.1 gl^{-1}). The carbon dosage range for the experiments was 0.2 to 5.0 mg and each experimental series contained 13 carbon dosages and a control without carbon. The initial concentrations of atrazine and MCPA were 100 μgl^{-1}. Samples (50 ml) for analysis were removed, through disposable 0.45 µm cellulose acetate filters, every 24 hours until equilibrium was achieved.

RESULTS AND DISCUSSION

Development of Procedures for Pesticide Analysis

DOM often causes analytical errors in the determination of organic micropollutants in natural waters. A comparisom has been made of the enrichment of pesticides with SPE and liquid-liquid extraction (LLE) from waters with a high content of DOM. The concentration of DOM was 10 mgl^{-1} as organic carbon (Johnson, 1991). They report that an interaction between pesticides and DOM occurs and leads to lower recoveries from SPE enrichment compared to LLE enrichment, although the difference was not statistically significant.

In this study DOM was found to be retained on the SPE column during the enrichment step and was observed as a brown to yellow layer on the top of the column. DOM also disturbs the HPLC-analysis because of high UV-absorption and the formation of a distinct frontal peak in the chromatogram. There is also the possibility of a decrease in separation capacity of the analytical column because of DOM irreversibly bound to the octadecyl silica. Therefore we considered it most satisfactory to attempt to reduce the amount of DOM in the final extract.

The naturally occurring DOM in lake water was used to allow a selection of the most suitable solvent for washing the SPE column before the elution of the isolates. Lake water was passed through a SPE column and then the column was extracted with different solutions.

TABLE 2. Pesticide recovery after washing of SPE column with different solutions

	Pesticide, % recovery				
Wash solution	MCPA	Dichlorprop	Mecoprop	Atrazine	Cyanazine
0.1M NaOH	59.4	80.3	85.1	-	-
H_2O:CH_3CN: CH_3OH 4:3:1	47.3	57.3	61.0	102.7	89.5
H_2O:CH_3CN 4:3	75.6	88.6	87.1	95.7	51.2

Experiments with lake water spiked with phenoxy acids showed that elution with water:acetonitrile (4:3) yielded the best recoveries. For the s-triazines it was found that water:acetonitrile:methanol (4:3:1) was suitable (Table 2).

One problem with using SPE columns is deciding whether they can be used once or several times. Two series of lake water spiked with phenoxy acids were tested. One series was tested with three enrichments in three different SPE columns and one series with only one SPE column to three enrichments. The results are shown in Table 3 where single use represents three different SPE columns and multiple use the same SPE column for three enrichments. Since the recoveries are similar for the two enrichment procedures, SPE columns can be used several times without carry-over or other errors.

TABLE 3. Pesticide recovery after single and multiple use of SPE columns

	Single use		Multiple use	
Pesticide	Recovery %	Confidence interval %	Recovery %	Confidence interval %
MCPA	99.7	12.3	89.2	9.3
Dichlorprop	96.1	10.6	89.7	1.3
Mecoprop	96.3	2.5	86.4	1.9
Atrazine	102.2	2.5	101.8	2.1
Cyanazine	89.5	1.9	88.0	1.9

The pH-dependence of the enrichment step was tested by adjusting the pH of lake water with concentrated HCl or 1 M NaOH. For the phenoxy acids, the pH range 2 to 5 was tested and for the s-triazines, pH 5 to 9. The best recoveries were obtained at pH 2 for phenoxy acids and at pH 7 for s-triazines. These results are important because they affect the sampling. A sample that has been acidified cannot be used for s-triazine analysis without pH-adjustment.

Adsorption Studies

The Freundlich isotherm equation has been found to satisfactorily describe the binding of organic micropollutants to AC (Sontheimer, 1988), and was therefore used in this study. The disadvantage is the concentration dependence for the constants, n and K. However, we always used the same initial concentration for each series of experiments and they are therefore comparable. In Fig. 1 the adsorption isotherm for atrazine in ultrapure water is shown. The isotherm lies within the 90% confidence interval, which is the second dashed line in the figure.

Adsorption isotherms for atrazine in lake water gave curved non-linear isotherms, Fig. 2, which made comparison difficult. From the literature this behaviour can be explained by competitive adsorption (Sontheimer,1988), or complexation to DOM, or a combination of both mechanisms (Pirbazari, 1992). At present it is difficult to resolve whether competitive adsorption or complexation is the more important process. Isolation of DOM in dialysis bags

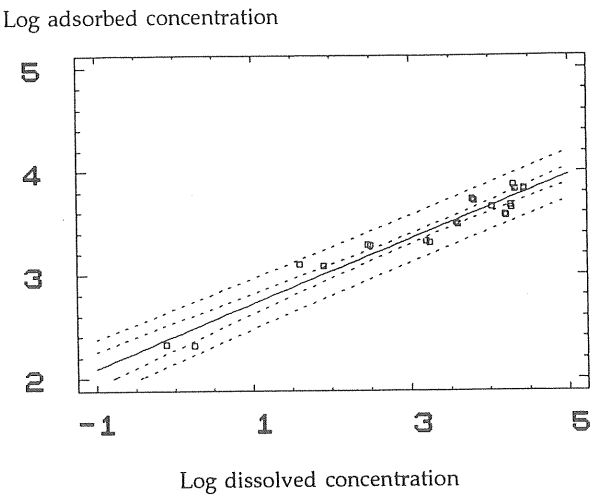

Fig. 1. Adsorption isotherm of atrazine in ultrapure water (C_0=100 $\mu g l^{-1}$, pH=7, equilibration time=24 hours). The 90% and 95% confidence intervals are shown as dashed lines.

(Pirbazari, 1992) is an unsatisfactory method for studying complexation as fulvic acids may pass through the membrane. Ultrafiltration has, though, shown that some degree of complexation for atrazine by soil-extracted humic substances exists (Wang, 1992). To study the competitive effect of DOM on the adsorption isotherm of atrazine the carbon would have to be preloaded with DOM and this should more closely resemble the situation in an AC filter in a treatment plant.

Atrazine adsorption can be more readily interpreted from plots of concentration versus carbon dosage, Fig. 3. The dissolved concentrations are lowest in the ultrapure water (the solid lines) and increase when DOM is present. It interesting to note that even removal of organic material with aluminium flocculation and AC filtration still leaves a surplus of DOM which reduces the adsorption capacity. This provides further evidence that competitive adsorption prevents atrazine removal, as individual pesticide complexing material might be expected to be removed in an AC filter. The results suggest that competitive adsorbants are in such a high initial concentration that they successfully compete even after AC filtration. It follows that the remaining difference in adsorption is due to a competitive adsorption rather than a complexation mechanism for atrazine. Sontheimer (1988) has shown that the higher dissolved concentrations are due to competitive adsorption in multi-component mixtures. The substances that are most weakly adsorbed on AC have a greater concentration in the water phase. However, this could also be interpreted as complexation of the pesticides with DOM in the water phase. Figure 3 also shows an increase in the dissolved concentration of atrazine in ozone treated water. Clearly, even a reduction in the molecular size of DOM does not reduce the interaction of DOM with atrazine.

A similar adsorption behaviour was found for MCPA added to lake water, Fig. 4. MCPA seems to have a weaker adsorption to AC compared to atrazine, because MCPA has a higher concentration in the water phase. In general, charged compounds are more weakly adsorbed to AC than neutral compounds. The adsorption of MCPA to AC is expected to depend on pH, the pK_a of MCPA being 3. The uncharged acid would adsorb better to AC than the charged, although DOM also changes charge and even configuration with pH and ionic

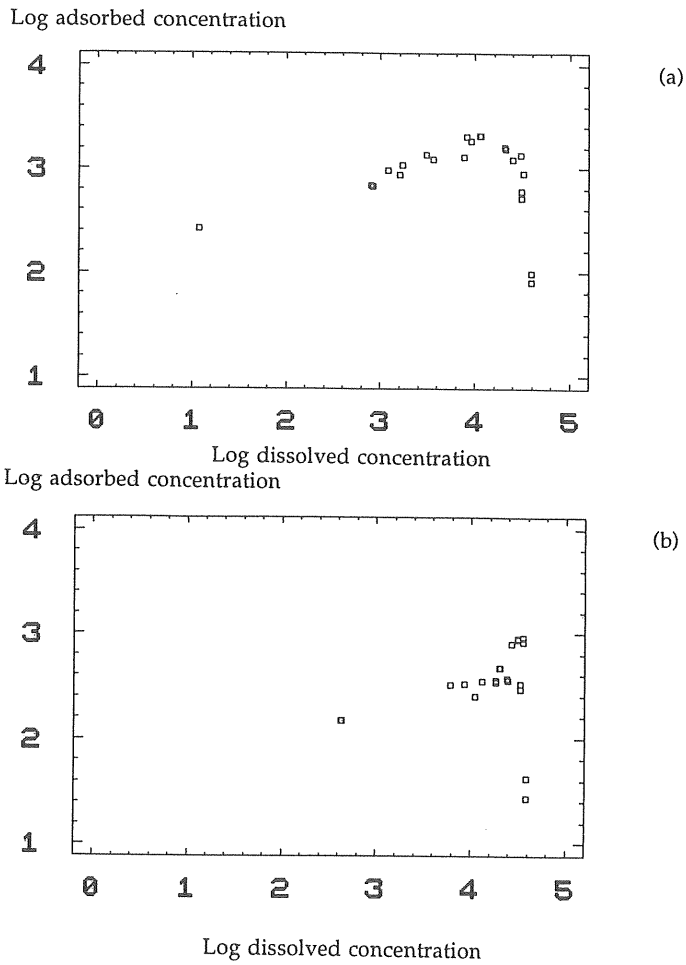

Fig. 2. Adsorption plots for (a) atrazine and (b) MCPA in lake water (C_0=100 $\mu g l^{-1}$, pH=7).

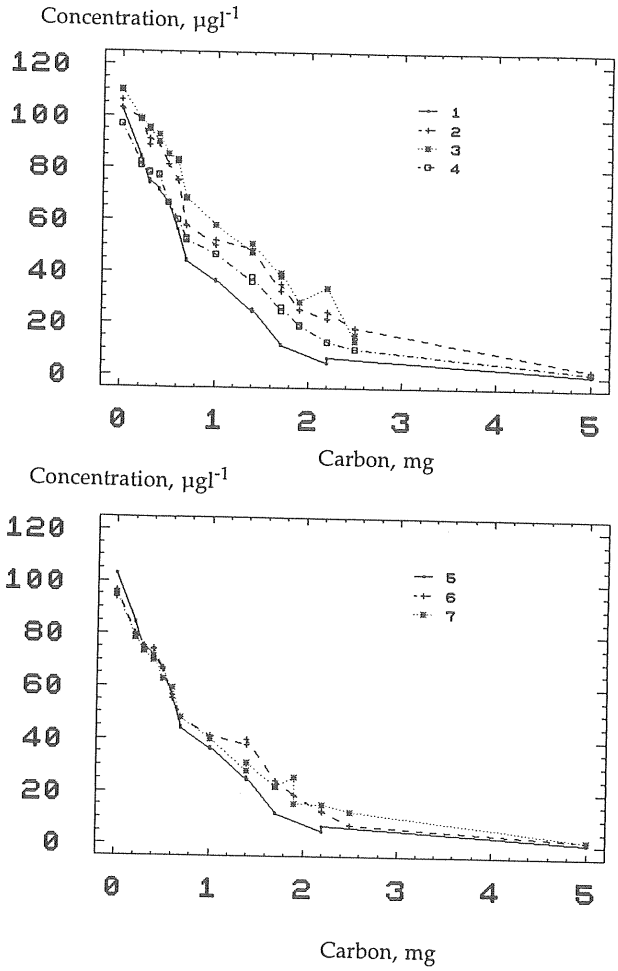

Fig. 3. Comparison of atrazine concentration versus carbon dosage plots (C_o=100 µgl^{-1}, pH=7, equilibration time=24 hours) for

1,5 Ultrapure water
2 Lake water
3 Lake water after aluminium flocculation
4 Lake water after aluminium flocculation and AC filtration
6 Lake water after ozone treatment
7 Lake water after ozone treatment, aluminium flocculation and sand filtration

strength. Elaboration of a discussion concerning the pH dependence of the adsorption of MCPA to AC in the presence of DOM therefore requires further experimentation. As phenoxy acids are the most widely used herbicides in Swedish agriculture, these results have important implications for the treatment of contaminated waters with AC. Further research would include removal conditions for phenoxy acids.

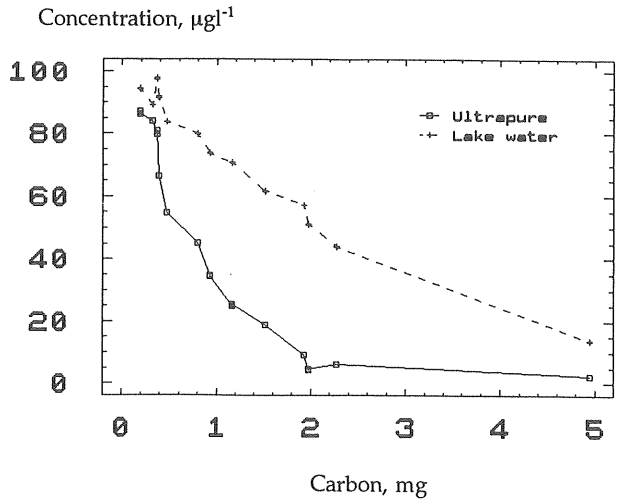

Fig. 4. Comparison of MCPA concentration versus carbon dosage plots. (C_0=100 µgl^{-1}, pH =7, equilibration time=24 hours.)

CONCLUSIONS

By selection of a suitable wash solution pesticides can be separated from DOM by SPE. This allows the analysis of phenoxy acids and s-triazines by HPLC.

DOM interferes with adsorption isotherms of atrazine and MCPA, in lake water and even after aluminium flocculation, AC filtration and ozone treatment. Possible mechanisms are competitive adsorption on AC, or complexation of the pesticides with DOM, or a combination of both. The adsorption of MCPA on AC is likely weaker than for atrazine, probably due to the charged chemical character of MCPA. The reduction of adsorption capacity of MCPA on AC in the presence of DOM is also greater than atrazine.

ACKNOWLEDGEMENT

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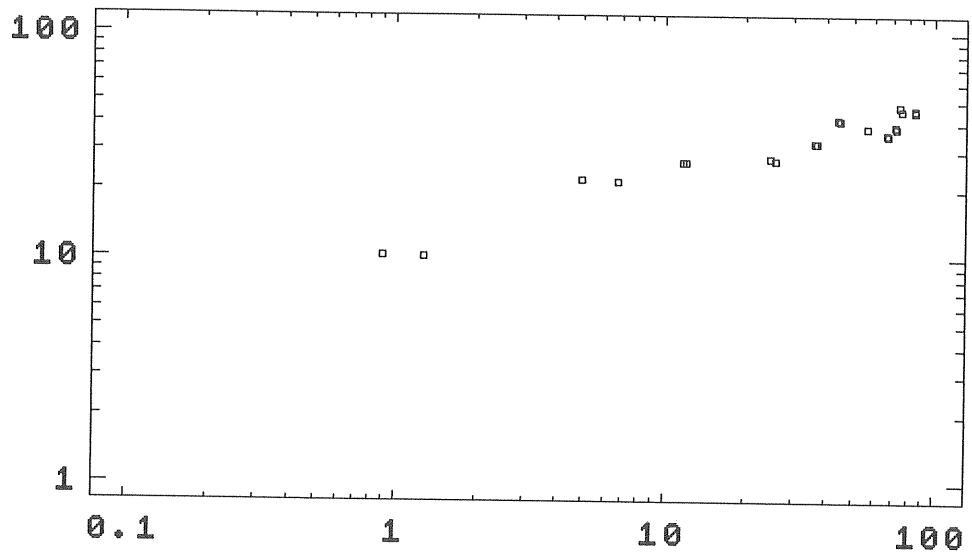
Adsorbed concentration $\mu g mg^{-1}$



Dissolved concentration $\mu g l^{-1}$

Fig. 1. Adsorption isotherm of atrazine in ultrapure water (C_o=100 $\mu g l^{-1}$, pH=7, equilibration time 24 hours).

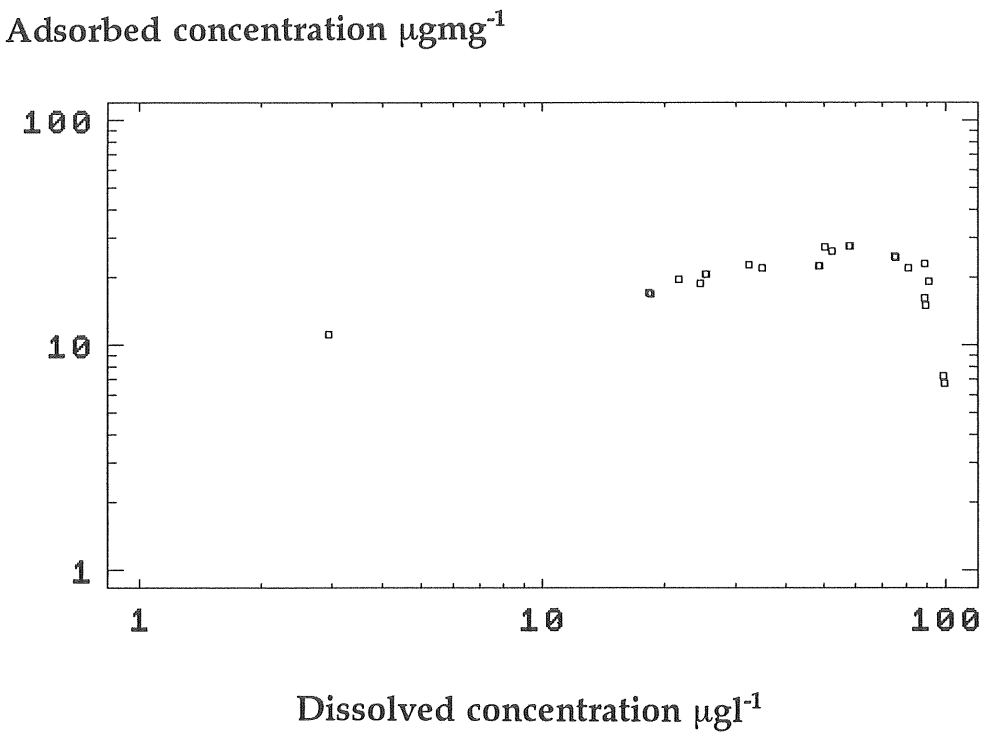


Fig.2a. Adsorption plot for atrazine in lake water (C_o=100 μgl^{-1}, pH=7, equilibration time 24 hours).

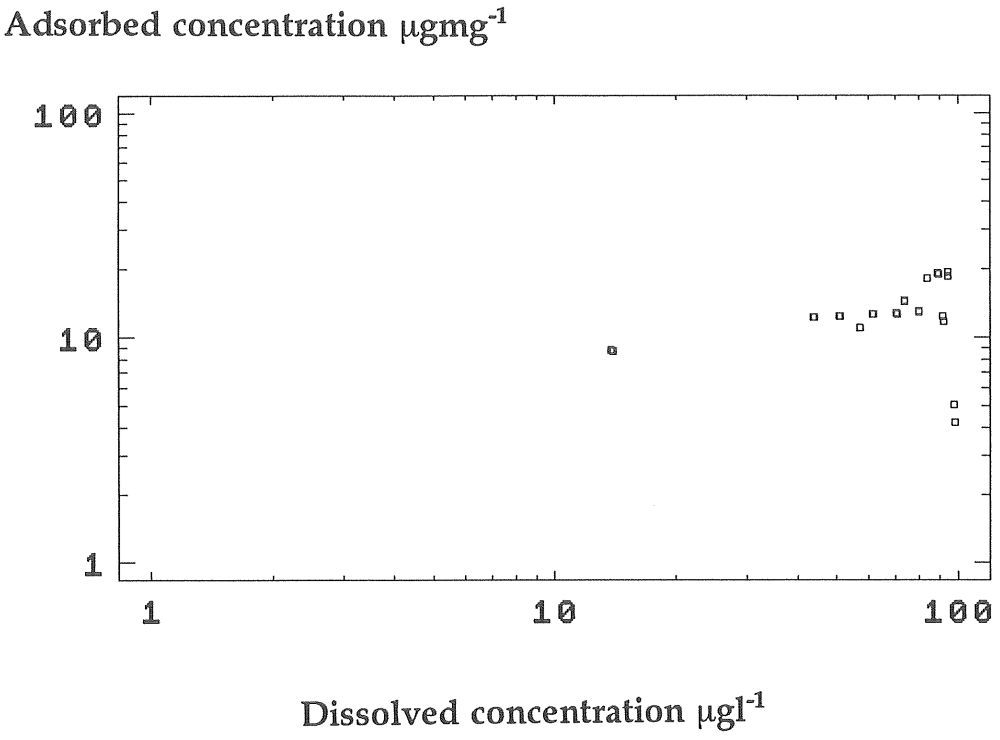


Fig. 2b. Adsorption plot for MCPA in lake water (C_o=100 μgl^{-1}, pH=7, equilibration time 24 hours).

3.2 Competitive interaction of natural organic matter and herbicides during adsorption to preloaded and non-preloaded granular activated carbon

In this study NOM preloading and competitive interaction of NOM and herbicides during adsorption to GAC were studied through a partitioning approach. For drinking water treatment, competitive interaction seems to be more critical in reducing the removal of herbicides than preloading with NOM. Preloading will cover adsorption sites but there are still sites left for herbicide adsorption.

COMPETITIVE INTERACTION OF NATURAL ORGANIC MATTER AND HERBICIDES DURING ADSORPTION TO PRELOADED AND NON-PRELOADED GRANULAR ACTIVATED CARBON

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ABSTRACT

Natural organic matter (NOM) preloading and the competitive interaction of NOM and herbicides during adsorption to granular activated carbon (GAC) were studied through a partitioning approach. Preloading reduced partition coefficient (K_D) values in single solute experiments with the adsorption of atrazine and MCPA to GAC. Competitive interaction was studied through NOM dilution experiments with non-preloaded and preloaded GAC. For both atrazine and MCPA, NOM competed significantly at raw water concentrations (~5 mgl^{-1} dissolved organic carbon). The K_D of atrazine increased gradually with NOM dilution, while no significant increase in K_D for MCPA was found until NOM dilution reached almost equimolar concentrations. Under treatment plant conditions NOM preloading will occur but there are still sites available for herbicide adsorption. However, NOM can compete for the remaining sites and it is likely that the character and concentration of NOM is critical for competitive interaction of herbicides for adsorption sites on GAC in a water treatment plant.

KEYWORDS: Competitive interaction, granular activated carbon, herbicides, partition coefficient, preloading.

INTRODUCTION

Adsorption of synthetic organic chemicals (SOC's) to granular activated carbon (GAC) represents an effective and protective technology for drinking water production, although it has been shown that natural organic matter (NOM) significantly reduces the adsorption of a wide range of SOC's (1-8). This is through a phenomenon known as "preloading" which can partly be explained by NOM intraparticle diffusion and adsorption to high energy sites in the GAC macropores and micropores and partly by NOM macromolecules becoming sterically lodged in micropores (3, 9). Certainly, a steady progression of earlier SOC breakthrough with time of NOM preloading has been demonstrated and this type of change in adsorption characteristics is a potential problem for scale-up and adsorption models which do not include preloading (9).

The effects of preloading and non-preloading for a range of SOC's can be studied through adsorption isotherms (1, 9, 10). Single solute adsorption to GAC is usually described through a Freundlich adsorption isotherm (1) where the heterogeneity parameter, n, increases towards a value of 1 with continued preloading (4, 11). NOM preloading is the major cause of reduced adsorption for chlorinated hydrocarbons (8, 12, 13). As herbicides are discharged seasonally and in highly variable concentrations into natural waters, preloading with NOM will significantly influence GAC performance and has therefore been extensively studied through Freundlich adsorption isotherms (14). However, adsorption isotherms are only applicable to single solutes in the absence of non-adsorbed NOM or other competing substances (1, 15). Competition of NOM with SOC's leads to reduction of adsorption capacity (16, 17) which becomes most apparent for polar solutes such as herbicides (2, 18). It is thought that competitive interaction involves either competitive adsorption with or SOC adsorption (or complexation) to humic

substances, or a combination of both (19).

An alternative to varying either available surface area (carbon dosage) or concentration of SOC is to consider dilutions of NOM in terms of partitioning, where the partition coefficient (K_D) is defined as the relationship between adsorbed SOC and dissolved concentration at equilibrium (20). K_D represents one point (q/C, adsorbed concentration/dissolved concentration) in a Freundlich adsorption plot and as with K_F (which is q where logC = 1, the adsorption capacity) will depend on initial concentration when pesticides are studied (21). It is also known that q varies with the volume/carbon ratio and therefore the experimental conditions for K_D should be well defined or a correction made (20). K_D can be considered a linear adsorption model while Freundlich is nonlinear (22). Here we investigate phase partitioning at varying NOM concentrations and although K_D will not predict adsorption capacity, it can describe the intensity of competitive interaction under a fixed experimental condition. The partitioning approach, which is considered here, allows the investigation of the competition interaction of SOC's (in this case herbicides) and NOM for non-preloaded and preloaded GAC down to and beyond equimolar (SOC:NOM) concentrations.

EXPERIMENTAL

Activated carbon preparation

The activated carbons selected for study were two GAC's, Filtrasorb 300 (Chemviron Carbon) and Aquasorb CX (Jacobi), and one pulverised activated carbon, GW (Chemviron Carbon). Filtrasorb 300 (GAC-1) and GW (PAC) are bituminous carbon and Aquasorb CX (GAC-2) is coconut-based. All activated carbons had high reported specific surface areas

(1000 - 1200 m^2g^{-1}) or iodine numbers (700 - 950). The GAC's were crushed in a mortar and passed through a 63 μm nylon sieve, dried in an oven at 110°C for 24 hours and stored in a desiccator until use. The GAC's were crushed to reduce the time required to reach equilibrium in the partitioning experiments (23, 24). PAC was dried and stored in a desiccator until use. For each experiment the crushed or pulverised activated carbon was weighed and suspended in ultrapure water (0.1 gl^{-1}) as a stock solution.

Preloading

GAC-2 was preloaded (in a Plexiglas column of 1m bed height) with finished drinking water from one of the drinking water treatment plants in Göteborg (Lackarebäck) with a content of dissolved organic carbon (DOC) of approximately 2 mgl^{-1}. GAC-1 was preloaded with sand-filtered lake water from lake Delsjön (the raw water source for the Lackarebäck treatment plant) with a DOC of 4-5 mgl^{-1}; two empty bed contact times (EBCT) were used, 5 min and 30 min. When the columns had reached NOM breakthrough, indicated through a negligible change in UV-absorbance at 254 nm between the inlet and outlet of the column, GAC samples were taken at the top of the columns. Sampled GAC was air-dried in an oven at 55°C to constant weight, crushed and sieved (< 63 μm), dried again at 55°C and stored in a desiccator until use.

Dilution experiments

Each experimental series was five dilutions of lake water together with controls of ultrapure water and undiluted lake water. Three initial concentrations of herbicide were tested (10, 50 or 100 μgl^{-1}) and the carbon amount (1.3 mg) was the same for all lake water dilutions. Ultrapure

water was Barnstead Nanopure and represented organic-free reference water. Lake water was collected from lake Delsjön, which is the drinking water source for Göteborg. Lake water was filtered through a glass fibre filter (GF/C Whatman) before use to remove heterogeneous suspended solids. For each experiment, filtered lake water was diluted with ultrapure water so that the DOC content varied between < 0.1 and 5 mgl^{-1}. For all dilutions, the pH was adjusted to 7 with phosphate buffer (0.01 M) and the volume made up to 0.5 l. The equilibration time was 24 hours. The DOC content for all dilutions was measured in a Shimadzu 5000 TOC analyser. The detection limit for DOC analysis was calculated from three standard deviations of the blank (ultrapure water) signal. Depending on instrument operation the detection limit was usually 0.1 mgl^{-1}, but could be up to 0.2 mgl^{-1}. The ultrapure water signal was below the detection limit.

Herbicide analysis

The two herbicides tested were a s-triazine, atrazine (4-ethylamino-6-chloro-2-isopropylamino-1,3,5-triazine) and a phenoxy acid, MCPA (4-chloro-2-methyl-phenoxy acetic acid). Stock solutions of 100 mgl^{-1} were prepared for each compound; in acetonitrile for atrazine and in methanol for MCPA. Solid-phase extraction (SPE) was used for enrichment of the herbicides from water before HPLC-analysis. SPE was on octadecyl-bonded silica (C_{18}) cartridges (Bond Elut, Varian) with methanol as eluent. A washing step (for atrazine; 50% water, 38% acetonitrile, 12% methanol and for MCPA; 55% water, 45% acetonitrile) before elution was developed to decrease the content of NOM in the extract injected into the HPLC instrument. HPLC-analysis was on a Waters system with 600E gradient pump, 700 Satellite WISP autoinjector, 490E multiwavelength UV/VIS detector and Maxima 825 chromatography workstation. Two HPLC methods were developed, one for each herbicide. In both methods the analytical column was C_{18}, 150 × 3.9 mm with 5 µm particles and detection through

UV-absorbance. For atrazine a NovaPak column (Waters) was used together with acetonitrile and ultrapure water (45%:55%) as mobile phase and detection at 220 nm. The acidic character of MCPA required a Resolve column (Waters) suitable for acids together with a mobile phase of methanol and 0.01 M phosphate buffer adjusted to pH 3.0 (60%:40%) and detection at 230 nm. The development of the SPE och HPLC procedures are described in full detail elsewhere (18).

RESULTS AND DISCUSSION

Preloading and single solute experiments

In Table 1, K_D is compared for non-preloaded and preloaded GAC-2 in ultrapure water. In these experiments the DOC concentration in the water was below the detection limit (0.1 mgl^{-1}) and single solute conditions are assumed. K_D for both herbicides shows a dependence on initial solute concentration; lower initial concentration gives higher K_D (1, 22). Lower initial concentration gives a higher relative solid-phase concentration for the same competing background, which implies that adsorption capacity improves when the initial concentration is lowered (1). It has been shown that the activated carbon surface has a limited number of high energy sites available for adsorption both for NOM and SOC's (3, 4). The difference in K_D for initial herbicide concentration therefore depends on competition by the solute itself with increasing competition at higher concentrations. Consequently, a low initial herbicide concentration results in higher K_D values.

The results in Table 1 are consistent with the findings of Haist-Gulde (2) for metazachlor (Table 2), however, the decrease in K_D is not as clear. This might be a result of the more pronounced

competitive effect from NOM, the DOC concentration for the distilled water used in those experiments being 0.3 mgl^{-1} (2).

Table 1. Single solute partitioning for non-preloaded and preloaded GAC-2 and two initial herbicide concentrations (10 and 100 μgl^{-1}).

	$K_{D'}$ lmg^{-1}	
	Non-preloaded	Preloaded
Atrazine (μgl^{-1})		
10	14	7.6
100	4.9	2.9
MCPA (μgl^{-1})		
10	8.5	5.5
100	1.9	0.7

Preloading leads to a significant reduction of K_D compared to non-preloaded activated carbon (Table 1). Preloading alters the energy distribution of the surface (3), the high energy sites being occupied first by NOM, while the target molecules, in this study herbicides, adsorb to sites with a lower energy. Surface heterogeneity decreases when the high energy sites are occupied and the amount that can be adsorbed onto the surface is also reduced. Consequently, in single-solute experiments, K_D decreases with increased NOM preloading and herbicide concentration.

Table 2. Single solute partitioning recalculated (2) for non-preloaded GW (PAC) and the herbicide metazachlor with different initial concentrations.

Metazachlor, μgl^{-1}	K_D, lmg^{-1}
10	2.1
20	2.0
50	1.5
100	1.9
150	1.2
400	0.6

Competitive interaction and dilution experiments

Dilution experiments were designed to follow the partitioning of herbicides with steadily decreasing concentrations of NOM. Experiments were carried out for three initial concentrations of atrazine and MCPA (Figure 1).

Atrazine has higher K_D values compared to MCPA and atrazine can therefore be regarded as more adsorbable than MCPA over a wide range of NOM concentrations. There is a significant difference in the shape of the NOM dilution curves for atrazine and MCPA, although both follow an exponential decrease of K_D with increasing NOM. Atrazine competes favourably for sites on the activated carbon even at relatively high NOM concentrations and therefore, the exponential decrease in K_D is prolonged. This is important for the use of PAC in a treatment plant (PAC can be added directly where a pollutant discharge is known or suspected) where effective atrazine removal will be obtained even at relatively high NOM concentrations (25).

This is not the case for MCPA where NOM almost completely prevents MCPA partitioning onto activated carbon at concentrations above 0.5 mgl^{-1} DOC. The NOM dilution curve for MCPA is steep between < 0.1 and 0.5 mgl^{-1} DOC and tails off to a low K_D value at DOC concentrations above 1 mgl^{-1}. The use of PAC to remove MCPA would therefore be restricted to groundwater supplies or surface water treatment plants where NOM concentrations are reduced to less than 1 mgl^{-1} DOC after treatment.

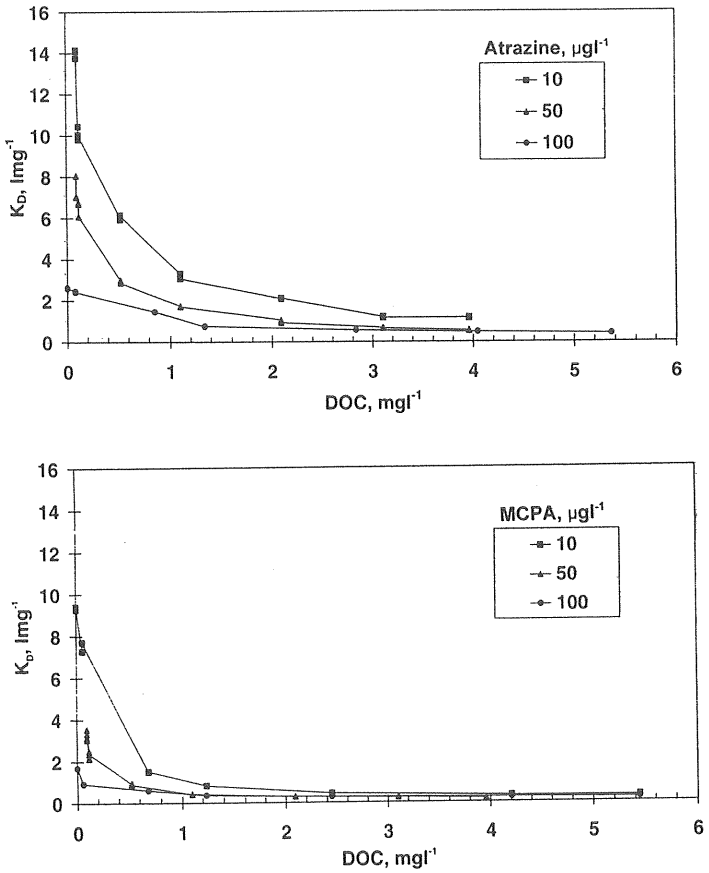

Figure 1. NOM dilution curves for atrazine and MCPA partitioning onto fresh GAC-1 at three initial concentrations, 10, 50 and 100 μgl^{-1}.

The difference in partitioning of atrazine and MCPA in the presence of NOM can be explained in terms of binding sites on activated carbon or in terms of NOM-herbicide interactions (3, 4). NOM binds weakly to the activated carbon surface whereas atrazine is more strongly adsorbed and can occupy the fresh high energy sites. With increasing NOM concentration the high energy sites become pre-occupied (in a similar way to preloading) by NOM and atrazine partitioning to the activated carbon surface is reduced (Figure 1). On the other hand, MCPA only favourably competes with NOM below approximately equimolar concentrations (assuming a molecular weight for NOM of 1 000 - 10 000). This can be explained by a similarity in affinity of MCPA and NOM for adsorption sites, thereby limiting effective MCPA adsorption to water with a low NOM content.

The difference in adsorption of atrazine and MCPA to activated carbon may relate to the chemical character of atrazine and MCPA. Atrazine is a weak base (26) and neutral at pH 7. MCPA is an acid with a pK_a of 3.05 (27) and is therefore charged at the pH prevalent in this study. However, in experiments where pH was varied between 3 and 9 (results not shown here) no difference in the adsorption of either atrazine or MCPA with pH to GAC-1 was found. Pesticides with higher water solubility, in this case MCPA, have been shown elsewhere (14) to have a lower removal efficiency on GAC and this probably accounts for the difference in adsorption characteristics of atrazine and MCPA.

A further explanation of the NOM dilution curves is that NOM retains atrazine or MCPA in solution through some form of complexation or adsorption. Several studies (28-31) have shown that atrazine can be complexed to humic substances, although the interaction is weak and probably the result of hydrogen bonding between atrazine and protonated carboxylic groups on humic substances. Complexation is pH dependent with the highest binding capacity in the

pH range of 2 - 4.5 (28, 30, 31), which corresponds to the pK_a of carboxylic acid groups on fulvic acid (FA) and humic acid (HA) (32, 33). The complexation of pesticides other than atrazine to humic substances has also been studied, including lindane (34) and glyphosate (35). The binding capacity showed the same pH dependence found for atrazine suggesting that the binding interaction is the result of protonation of carboxylic groups on the humic material. In natural waters with a neutral pH this complexation should be of minor importance for atrazine since the atrazine-FA complex is not measurable above pH 5.5 and the binding capacity of atrazine to HA decreases rapidly in the pH range that is normal in natural waters, being negligible at pH 7.8 (30). Retention of atrazine in solution is not therefore a likely explanation of the competitive interaction observed here. Phenoxy acids appear to have been overlooked in studies of interactions with NOM.

Competitive interaction and activated carbons

NOM dilution curves for the three non-preloaded activated carbons demonstrated similar curves for atrazine for the two GAC's, but lower values for the PAC (Figure 2). The two GAC's were crushed and treated identically, but have different reported surface areas (GAC-1, 1200 m^2g^{-1}: GAC-2, 1000 m^2g^{-1}) and are prepared from different materials (GAC-1, bituminous coal: GAC-2, coconut shells). This suggests that competitive interaction, rather than adsorption site availability and type, limits the partitioning of atrazine and MCPA in the presence of NOM.

The lower results for PAC may be related to a different preparation of GAC (crushed and sieved) from PAC (used directly). The K_D values reported here assume equilibrium after 24h equilibration. In preliminary experiments, we found little change in dissolved herbicide

concentration after 24h equilibration with GAC crushed and sieved to < 63 μm (18). Elsewhere (23, 24) it has been shown that true equilibrium can take weeks or months and that grain size will have a significant effect on equilibration time. It is acceptable to measure K_D after a stated time as long as all conditions are reported, *i.e.* the K_D is operationally defined. Comparison of partitioning between activated carbons therefore demands similar preparation.

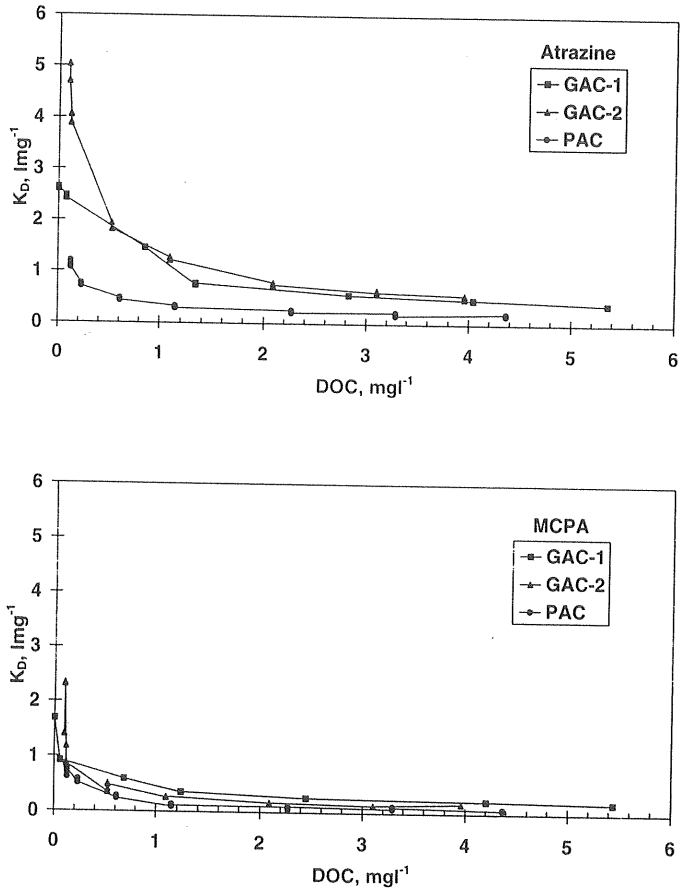

Figure 2. NOM dilution curves of atrazine and MCPA (100 μgl^{-1}) for GAC-1, GAC-2 and PAC.

Competitive interaction and preloading

A comparison was made between preloaded and non-preloaded GAC-2 for NOM dilution curves at concentrations of 10 and 100 μgl^{-1} for both atrazine (Figure 3a) and MCPA (Figure 3b). Preloading was found to significantly reduce partitioning for atrazine, particularly at low concentrations of NOM. Preloading fills high energy sites (3) which atrazine would otherwise successfully compete with NOM for.

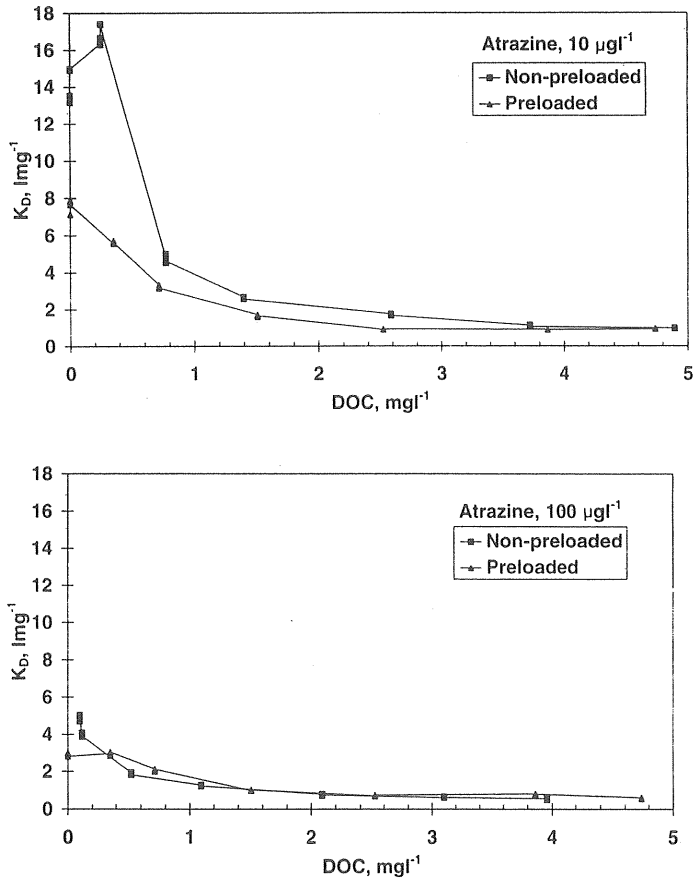

Figure 3a. NOM dilution curves for atrazine at preloaded and non-preloaded GAC-2.

At higher NOM and atrazine concentrations (Figure 3a), preloading has little effect compared to competitive interaction for atrazine, while for MCPA (Figure 3b) competitive interaction dominates the NOM dilution curve down to 0.5 mgl^{-1} DOC.

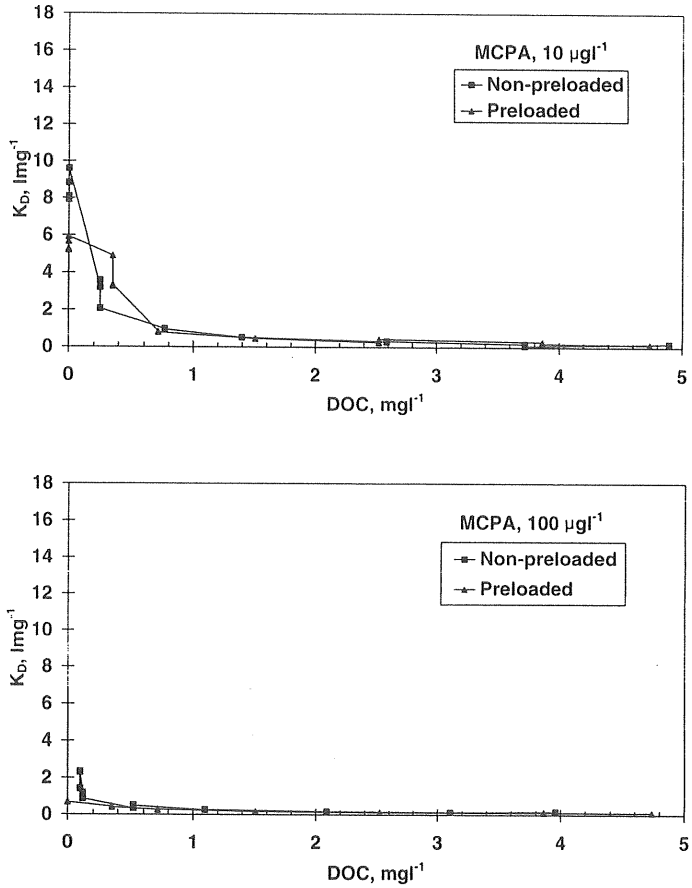

Figure 3b. NOM dilution curves for MCPA at preloaded and non-preloaded GAC-2.

GAC-1 was preloaded with sand-filtered lake water for two EBCT's, 5 and 30 minutes. In Figure 4 the NOM dilution curves for non-preloaded and preloaded GAC-1 are compared at the same atrazine concentration (10 μgl^{-1}) and demonstrate that EBCT has no effect on preloading when breakthrough has occurred. An interpretation of these results is that a change in NOM loading conditions for a GAC filter-bed will have little effect on herbicide partitioning. This is surprising because an optimal DOC removal has been shown for an EBCT of 20-30 minutes (36). However, the type of NOM used for preloading seems to have an effect, different waters were used to preload GAC-1 and GAC-2. The K_D of atrazine for non-preloaded GAC (Figure 4) is the same as for GAC-2 (Figure 3a) at 10 μgl^{-1}, but with the preloaded carbon, K_D decreases to around 2 for GAC-1 compared to 7.6 for GAC-2. GAC-1 was preloaded with sand-filtered lake water while GAC-2 was preloaded with finished drinking water. It has been demonstrated elsewhere (36) that conventional treatment removes the most strongly (by GAC) adsorbed fictive component of NOM in raw water, fictive component analysis separates NOM into a mixture of fractions based on different adsorbabilities to activated carbon (1, 36, 37). Therefore, for GAC-2 which was preloaded with finished drinking water, the absence of the strongly adsorbed component allows a greater adsorption to GAC-2 for atrazine. This is demonstrated through higher K_D values (Figure 3a) at DOC concentrations below 0.5 mgl^{-1} compared to preloading with sand-filtered lake water (Figure 4). An alternative approach is to characterise NOM through the competitive effect of NOM with adsorption of a SOC to activated carbon (5). This competitive effect is calculated as a single compound termed the equivalent background compound (EBC).

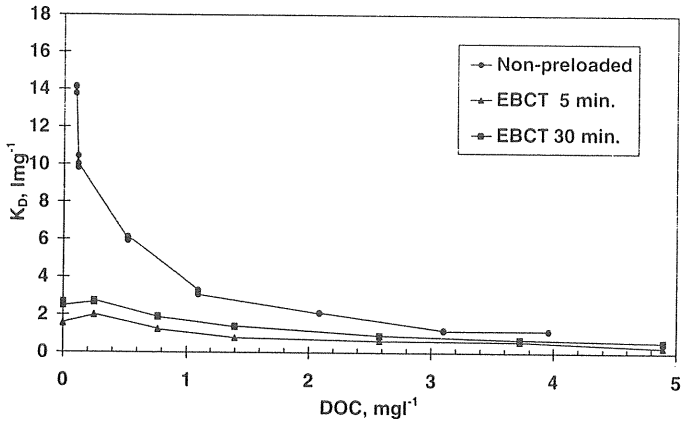

Figure 4. Effect of EBCT for preloaded GAC-1 on the NOM dilution curve for atrazine (10 μgl^{-1}) and compared to non-preloaded GAC-1.

For drinking water treatment, competitive interaction seems to be more critical in reducing the removal of herbicides than preloading with NOM. Preloading will cover adsorption sites but there are still sites left for herbicide adsorption. There is an urgent need for more extensive studies of the effect of preloading of GAC with NOM of different characteristics and origin. However, the competitive nature of NOM is critical in partitioning as this will determine whether adsorption of herbicides can still occur. NOM dilution curves give useful comparative information where the experimental conditions are well-defined.

It may seem from this study, after considering preloading and competitive interaction, that there is an unacceptable loss of herbicide removal efficiency of activated carbon compared to that reported for fresh carbon. Conventional treatment technology in waterworks, such as chemical flocculation, rapid sand filtration and chlorination, have been shown to have little

effect on trace herbicide concentrations (38). However, slow sand filtration has recently shown satisfactory removal of some herbicides, especially phenoxy acids (39), although treatment through oxidation, *e.g.* ozonation, and removal on activated carbon have shown better results for atrazine (40, 41). However, oxidation can result in the formation of unwanted by-products. The ozonation of atrazine produces deethylatrazine, although both atrazine and deethylatrazine can be removed by activated carbon (40). Ozonation of humic substances gives smaller, more polar molecules such as aldehydes and carboxylic acids (42, 43). Adsorption of herbicides to activated carbon has the advantage over ozonation that no by-products are formed and that no chemicals are added during treatment. Although preloading and competitive interactions with NOM have been shown here to significantly reduce the removal of herbicides, biological activity in a GAC column might improve removal through biodegradation, as found for MCPA in slow sand filtration (39). Increasingly stringent regulations on permissible, and on sporadic variations of, herbicide concentrations in drinking water may only be met by activated carbon adsorption (12). Therefore GAC still represents the best water treatment alternative for herbicides, although the placement of GAC in the plant is critical for the effective removal of herbicides. It is possible to assess the intensity of competitive interaction by partitioning spiked herbicides and NOM in samples (through a treatment plant) onto preloaded GAC and thereby determine the effective adsorption of herbicides onto GAC. It is important to preload with the NOM of interest because it has been shown that the effects of NOM preloading on the Freundlich coefficient and heterogeneity parameter are natural water specific (11). These studies could provide preliminary design information and it is known that small-scale columns can be used to selectively screen GAC's prior to pilot-scale testing (44). This is a continuing focus of our research.

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3.3 Removal of UV-absorbance and TOC characterised NOM in columns of granular activated carbon

This study was presented at the Natural Organic Matter Workshop: Influence of natural organic matter characteristics on drinking water treatment and quality, 18-19 September, 1996, Poitiers, France. Here the NOM were characterised as UV absorbance and total organic carbon (TOC) and competitive interactions of the NOM components were studied in pilot columns of granular activated carbon. Sampling ports through the GAC columns provided profiles of UV and TOC removal that showed the preferential removal of UV absorbing NOM compared to TOC characterised NOM.

REMOVAL OF UV-ABSORBANCE AND TOC CHARACTERISED NOM IN COLUMNS OF GRANULAR ACTIVATED CARBON

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ABSTRACT

The competitive interactions of UV-absorbing and non-absorbing NOM (natural organic material) were studied in pilot columns of GAC (granular activated carbon). Sampling ports through the columns provided SUVA (Specific UV Absorbance) profiles and demonstrated the preferential removal of humic (UV_{254}) and lignin-type (UV_{265}, UV_{280}) substances compared to TOC characterised NOM. EBCT (empty bed contact time) has a significant effect on depth profiles. GAC type is also important for the extent of competitive interactions between NOM components.

INTRODUCTION

The removal of anthropogenic, particularly toxic, organics is an important consideration for water treatment and granular activated carbon (GAC) represents an effective technology for the removal of organic compounds. It is known that natural organic material (NOM) is simultaneously removed by GAC and decreases the adsorption capacity of GAC for other organic compounds, although few studies have carefully considered the removal of components of NOM through GAC columns.

In this study NOM is characterised as total organic carbon (TOC) and as UV absorbance at three wavelengths 254, 265 and 280 nm. The wavelength of 254 nm is commonly used for measurement of aquatic humic substances and the choice of wavelength is operational because it corresponds to the sharp spectral line of a low-pressure mercury lamp (Dobbs *et al* 1972). Wavelengths of 265 and 280 nm are used for the semi-quantitative analysis of lignin-type substances in water (Lawrence 1980).

Specific UV absorbance (SUVA) is also used in this study for the characterisation of NOM. SUVA is defined as the ratio of UV absorbance at 254 nm to the TOC content and is expressed as $m^{-1}/mg\ l^{-1}$. Empirically it has been shown that an increase in SUVA value corresponds to more aromatic structures of NOM compared to lower SUVA values (Edzwald and van Benschoten 1990). SUVA values of 4-5 indicate the presence of hydrophobic, aromatic, aquatic humic material with high molecular weight while SUVA values under 3 indicate that NOM is largely of non-humic character, more hydrophilic and less aromatic compared to waters with higher SUVA values.

These experiments demonstrate the importance of careful choice and testing of GAC for the removal of NOM and pollutants in the presence of NOM. Breakthrough of NOM is shown to be a critical parameter in GAC function.

EXPERIMENTAL

Pilot plant

The GAC's selected for this study were Filtrasorb 300 (Chemviron), Aquasorb BG-09 (Jacobi AB) and Aquasorb CX (Jacobi AB). Filtrasorb 300 (GAC-1) and Aquasorb BG-09 (GAC-2) are bituminous carbon and Aquasorb CX (GAC-3) is coconut-based. The specific surface areas are high, 950-1200 m^2g^{-1}. The GAC's were used as delivered without further treatment.

The columns were of Plexiglas with a internal diameter of 12.5 cm and a total height of 2.5 m operated in a down-flow manner. The GAC bed height was 1m with six sampling ports placed at different bed depths. Two empty bed contact times were used, 5 and 30 minutes. The columns were back-washed after each sampling occasion. The feed water was sand-filtered water from lake Delsjön, a raw water source for the city of Göteborg. The sand filter was back-washed with the same frequency as the GAC columns.

Measurement

Ultraviolet (UV) absorbance was measured directly at the pilot plant while samples for TOC analysis were transported to the laboratory. UV-absorbance was measured for each sampling occasion on a Zeiss instrument in a 5 cm flow-through quartz cell. The wavelengths used for characterisation of NOM were 254, 265 and 280 nm. The TOC measurements were in a Shimadzu 5000 TOC analyser. Ultrapure water was Barnstead Nanopure and represented organic-free reference water for determinations of both UV-absorbance and TOC.

RESULTS AND DISCUSSION

Competitive interaction of UV_{254} absorbing NOM with non-absorbing NOM for adsorption sites is indicated in SUVA depth profiles (figure 1). The SUVA profiles demonstrate the preferential adsorption of the UV_{254} absorbing component of NOM compared to TOC characterised NOM down the GAC column. Similar findings has been reported elsewhere for other conventional water treatment technologies (Edzwald *et al* 1985). Sharp removal gradients for both UV_{254} and TOC are found in the first 10 cm of the column and move down the column with time (figures 2 and 3), occupying available adsorption sites and blocking micropores. No difference was observed in SUVA profiles for the other selected UV absorption wavelengths (not shown) which indicates that humic substances (254 nm) are removed to the same extent as lignin-type substances (265 and 280 nm). This is not surprising as hydrophilic, aromatic humic substances compete favourably for adsorption sites on GAC and the macromolecular aromatic structure of lignin would be expected to provide similar adsorption properties. Molecular size will also influence the competitive adsorption of UV absorbing NOM with solution characteristics before adsorption having a significant effect (Kilduff *et al* 1996). The competitively adsorbing component observed here through the SUVA profiles are therefore probably the small, hydrophobic aromatic substances of NOM.

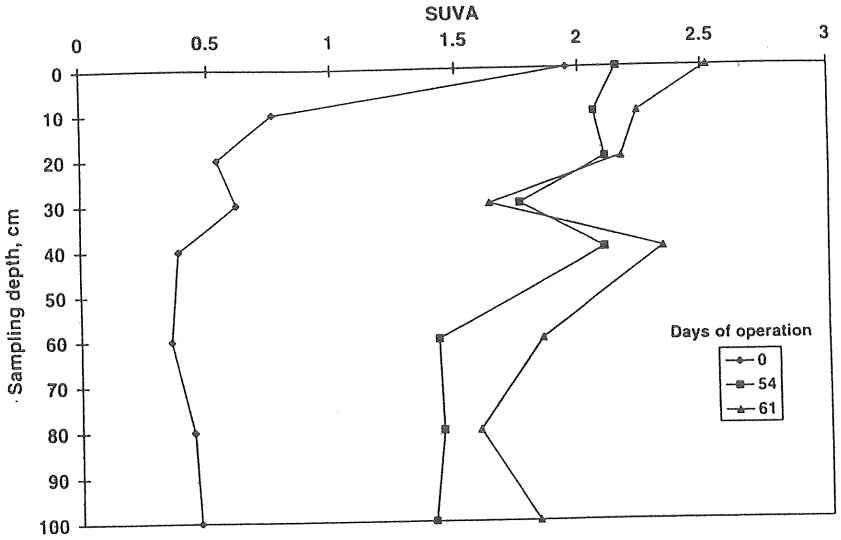

Figure 1. SUVA profile for GAC-1 with 30 minute EBCT.

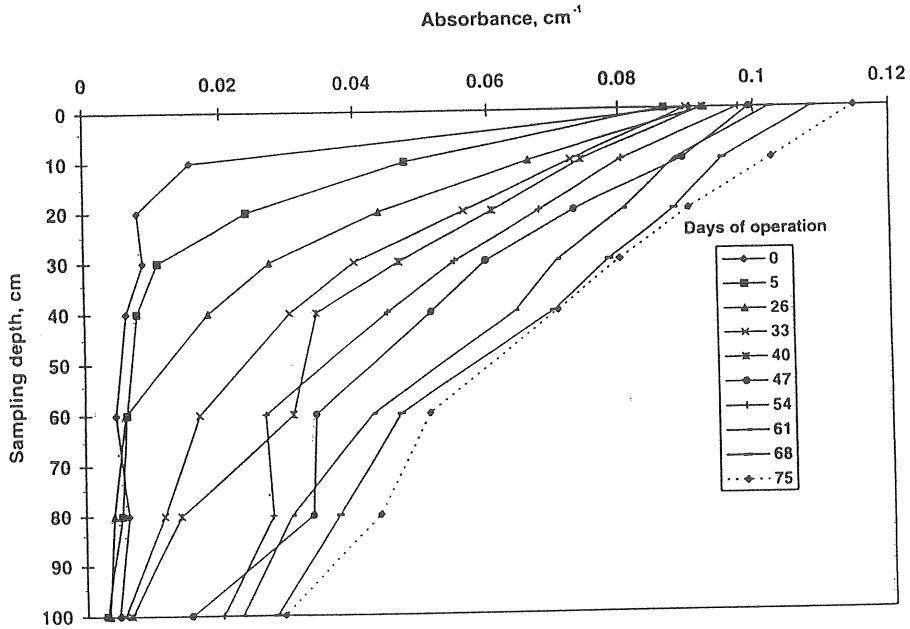

Figure 2. Absorbance profile (254 nm) for GAC-1 with 30 minute EBCT.

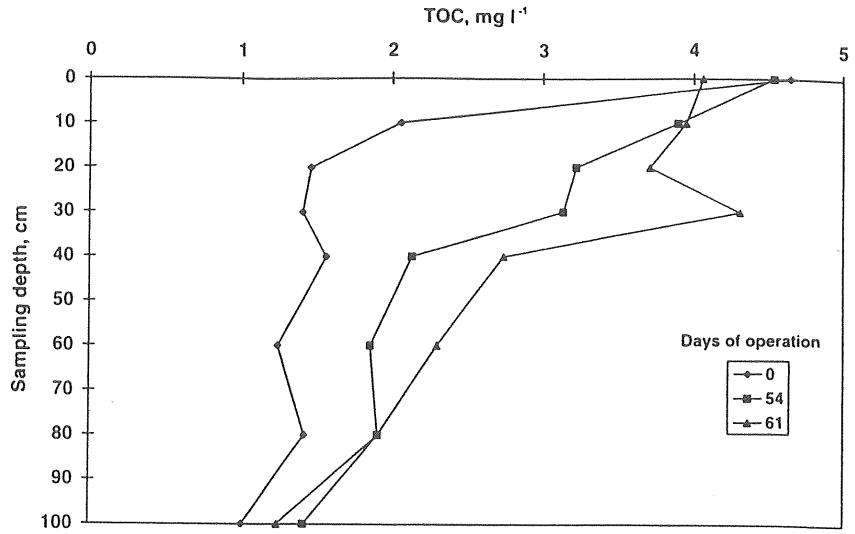

Figure 3. TOC profile for GAC-1 with 30 minute EBCT

The removal of NOM is dependent on empty bed contact time (EBCT) and carbon type. GAC-2 showed breakthrough before 26 days for a 5 minute EBCT (figure 4), while for a 30 minute EBCT (figure 5) the breakthrough occurred before 47 days of operation. After breakthrough, EBCT had no effect on NOM removal. This agrees with the findings of Crittenden *et al* (1993) that the optimum EBCT to achieve a treatment objective of 1 mg l^{-1} DOC is 20-30 minutes.

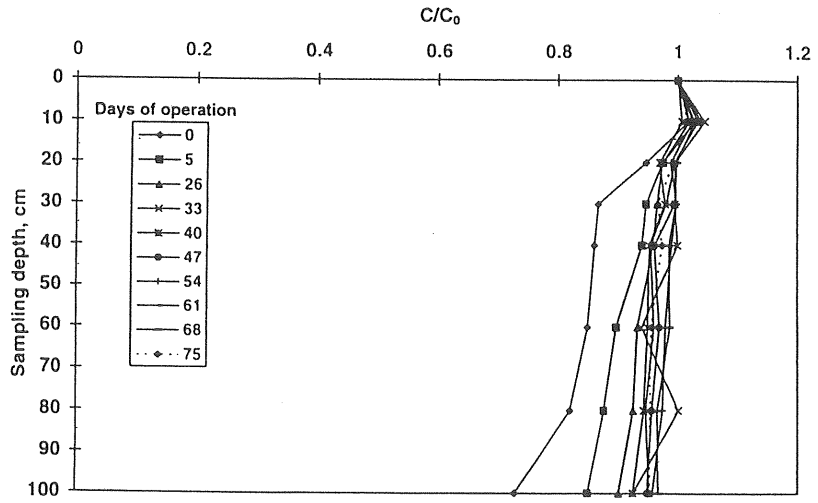

Figure 4. Profiles of C/C_0 (UV_{254}) for GAC-2 with 5 minute EBCT.

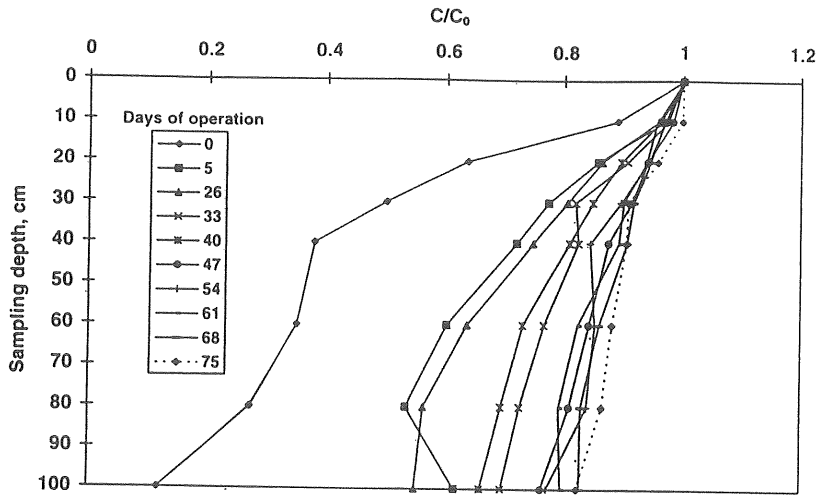

Figure 5. Profiles of C/C_0 (UV_{254}) for GAC-2 with 30 minute EBCT.

The carbon type has an effect on breakthrough of NOM both when measured as UV and TOC because the three GAC's used in this study showed different breakthrough curves although the exact reason for this is not obvious. The parameters used for describing GAC, for example raw material, specific surface area and pore size distribution do not give a clear answer. The theory of site energy distributions on the GAC surface is probably more adequate to explain differences between GAC adsorption capacity (Derylo-Marczewska *et al* 1984).

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3.4 Competition of natural organic matter and atrazine for adsorption to preloaded granular activated carbon in drinking water treatment

This study describes preloading and competitive interaction phenomena for atrazine with NOM. The investigations were on granular activated carbon preloaded in minicolumns. High-performance size exclusion was used for fractionation of the NOM through a drinking water treatment plant and in ground water and showed that the competing NOM fraction is of low molecular weight and refractory during water treatment.

Competition of natural organic matter and atrazine for adsorption to preloaded granular activated carbon in drinking water treatment

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Abstract

The effects of preloading and competitive interaction of natural organic matter (NOM) on atrazine adsorption was studied for crushed granular activated carbon. Changes in the Freundlich adsorption parameters K_F and n demonstrated the significance of competitive interaction during adsorption. High-performance size exclusion chromatography coupled to UV and fluorescence detection in tandem, demonstrated that the competing NOM fraction is low molecular weight and refractory during water treatment. This ubiquitous NOM fraction, found in both surface water and groundwater, appears to be responsible for preloading with little difference in atrazine adsorption characteristics for the same preloading conditions. This NOM fraction is also implicated in competitive interaction, which was found to override preloading effects through drinking water treatment.

Keywords: Competitive interaction, preloading, granular activated carbon, atrazine, natural organic matter.

Introduction

The presence of pesticides in the aquatic environment represents a seasonal threat to quality directives for drinking water supplies. Of particular concern are the triazine and the phenoxy acid herbicides, some of which are relatively water soluble and are sufficiently persistent to be found at $\mu g l^{-1}$ concentrations in surface and groundwaters (*1,2,3*).

Conventional water treatment technologies, including clarification, rapid sand filtration, softening and chlorination are ineffective in the removal of pesticides (*4*). Attention has therefore turned to adsorption on activated carbon as both granular (GAC) and powdered (PAC) forms, biodegradation by slow sand filtration and ozone destruction (*5*). These three technologies have proved effective for pesticide removal, although concern over possible by-products from slow sand filtration and ozone treatment has meant that irreversible adsorption to activated carbon has been considered the Best Available Technology. Additionally, activated carbon can be employed for a wide range of dissolved pesticides with varying chemical properties. GAC is usually preferred as it is cost-effective and covers sporadic unexpected discharges of pesticides which might be missed by PAC dosage (*4*).

However, natural organic matter (NOM) has been demonstrated to significantly affect pesticide and other synthetic organic chemicals (SOC's) adsorption to GAC through a

phenomenon which is usually termed preloading. Preloading involves weak but irreversible adsorption of NOM onto GAC ahead of a target SOC on a GAC column (*6*). Preloading with NOM leads to a significant decrease in adsorption capacity (Freundlich K_F), a reduction of the heterogeneity of adsorption sites (Freundlich n) and a slowing of adsorption kinetics (*6,7,8*). Consequently, it is now well recognised that Freundlich adsorption isotherms for SOC's carried out at unrealistically high SOC concentrations and which ignore the competitive effect of NOM on SOC adsorption, are unsuitable for the prediction of GAC filtration performance in a water treatment plant (*9*).

A number of studies have shown that Freundlich adsorption isotherms conducted with preloaded GAC (*9,10*) and results from preloaded microcolumns (*6*) can provide a reasonable prediction of capacity reduction and breakthrough in GAC columns. Combining ideal adsorbed solution theory, IAST, with the effects of NOM preloading calculated as a single equivalent background compound, EBC, allows the modelling and prediction of GAC performance (*8,9*).

Progress in understanding the mechanism of preloading has been hindered by difficulties in characterising NOM in natural waters. Characterisation techniques involving isolation procedures (*11*) are likely to alter the NOM properties. UV-absorbance and fluorescence are properties of NOM which are non-destructive and sufficiently sensitive for direct detection in natural waters (*12*), although they provide no information on molecular weight (MW) which is a critical property for determining the extent of competitive interactions of NOM and SOC's in the deeper micropores of GAC (*13,14*).

Developments in ultrafiltration and high-performance size exclusion chromatography (HPSEC) combined with UV absorption and fluorescence now allow more detailed studies of variations of NOM characteristics with MW (*15,16,17*). Artifacts in HPSEC have been avoided by the choice of appropriate standards such as the random coil polymers, polystyrene sulphonates - PSS (*18*). Consequently, it is now believed that NOM is less polydisperse and smaller (MW 840 - 2 300) than previously proposed (*16*) and should therefore penetrate into the deeper GAC micropores; a pore blockage mechanism is therefore not required to account for preloading. Indeed, there is increasing evidence that the small molecular size components of NOM are adsorbed preferentially to activated carbon and that these are the only preloading components showing any significant effect on SOC adsorption to GAC (*19*). These interferring components have been found in an ultrafilterable (< 3 000 MW) fraction of surface water and have been identified by HPSEC as NOM of MW 1 000 - 1 400 (*19*). On the other hand, the component interferring with 2-methylisoborneol adsorption has been found in a smaller ultrafilterable (< 500 MW) fraction (*17*). A difficulty in interpreting the ultrafiltration findings is that the MW cut-off is nominal and therefore does not provide the precision required for understanding NOM interference in GAC adsorption. A further complexity is the competitive interaction of NOM and SOC's during adsorption to preloaded GAC (*20*). For drinking water treatment, competitive interaction seems to be more critical in reducing the removal of herbicides than preloading with NOM.

This study focuses on the competitive interaction of atrazine and NOM through drinking water treatment plants. HPSEC with tandem UV-fluorescence detection is used to characterise NOM and provides explanations for the competitive interaction of atrazine in

spiked water samples and GAC preloaded in minicolumns.

Experimental

Water samples

Water samples were collected in polyethylene bottles, filtered through a glass fibre filter (GF/C, Whatman) and stored at 4°C until analysis. Two surface waters (lake Finnsjön and lake Delsjön), used as sources for drinking water treatment, and one groundwater (Gräfsnäs) used as drinking water after aeration, $KMnO_4$ oxidation and contact with a limestone filter, were investigated and the water quality characteristics are presented in Table 1.

Table 1 Water quality characteristics.

Water source	DOC*, mgl^{-1}	abs_{254}, cm^{-1}	abs_{254}/DOC*	Ca, mgl^{-1}	Mg, mgl^{-1}	Alkalinity as HCO_3^{-1}, mgl^{-1}	pH
Finnsjön	4.37	0.098	2.24	7.54	1.38	12	6.7
Delsjön	4.58	0.104	2.27	7.71	1.86	16	7.1
Gräfsnäs	0.55	0.015	0.03	41.1	9.80	188	8.0

* DOC= Dissolved organic carbon, measured on a Shimadzu 5000 TOC analyzer.

Water samples were also collected through two treatment trains. The Finnsjön plant involves chemical treatment with alumninum sulphate (55 g m^{-3}) including direct filtration in continuous filters, followed by slow sand or GAC filtration. The Lackarebäck (lake Delsjön source) plant involves chemical treatment with aluminium sulphate (40 g m^{-3}) including coagulation, flocculation, sedimentation (flotation - pilot scale) and GAC filtration.

High-performance size exclusion chromatography (HPSEC)

HPSEC was used to examine the molecular weight distributions in the treated and untreated, surface and groundwaters without any concentration or fractionation step prior to HPSEC analysis. The analytical column was a Phenomenex BioSep-SEC-S2000 (hydrophilic bonded silica) 300 x 7.5 mm with a guard column 75 x 7.5 mm of the same stationary phase to protect the analytical column. The mobile phase was 0.02 M phosphate buffer at pH 6.8 with a flow rate of 0.5 ml min^{-1} and the injection volumes were 100 or 200 µl. UV detection was at 220 nm, while fluorescence had a 350 nm excitation wavelength and a 450 nm emission wavelength. HPSEC analysis was on a Waters system with a 600E gradient pump, 700 satellite WISP autoinjector, 490E multiwavelength UV/VIS detector, 470 scanning fluorescence detector and Maxima 825 chromatography workstation. Calibration was carried out with polystyrene sulphonate (PSS) standards (Polymer Standard Service, USA) with weight average molecular weights of 1 430, 4 300, 6 780 and 16 800. The concentration of each PSS standard was 200 mg l^{-1} dissolved in the mobile phase.

Atrazine analysis

The herbicide tested was the s-triazine, atrazine (4-ethylamino-6-chloro-2-isopropylamino-1,3,5-triazine). A stock solution of 100 $\mu g l^{-1}$ was prepared in acetonitrile. Solid-phase extraction (SPE) was used for enrichment from water before analysis with high-performance liquid chromatography (HPLC); HPLC was on the same Waters system as described previously for HPSEC. Octadecyl bonded silica (C_{18}) cartridges (Bond Elut, Varian) were used together with methanol as eluent. A washing step with a solution of 50% water, 38% acetonitrile and 12% methanol before elution was developed to decrease the content of NOM in the extract injected into the HPLC instrument. The HPLC analytical column was NovaPak C_{18} (Waters), 150 x 3.9 mm with 5 µm particles, used together with acetonitrile and ultrapure water (45%:55%) as mobile phase and UV-detection at 220 nm.

GAC preparation and preloading conditions

The GAC selected for this study was Filtrasorb 300 (Chemviron Carbon) which is produced from bituminous carbon and has a reported specific surface area of 1000 $m^2 g^{-1}$. The GAC was crushed in a mortar, sieved and the fraction of 74-125 µm was used in the study. This was the smallest fraction providing a reasonable flow through the minicolumns. 0.5 g was packed into an empty (fresh) SPE column. Polyethylene frits (20 µm) retained the GAC in the SPE column (minicolumn). GAC was then preloaded with water, 4 l for untreated water and 10 l for treated water. Water was fed under gravity and preloading took one to three weeks. The extent of preloading was followed by measuring abs_{254} in the outflow. After preloading, the minicolumns were emptied and the carbon was dried in an oven at 55 °C for 24h and stored in a desiccator until use. A reference preloaded GAC was prepared with 10 l of water from lake Delsjön and used through all studies for comparison.

Adsorption experiments with PSS standards

The aim of these experiments was to study the competitive effects when the organic background is known in terms of chemical structure, MW and concentration. Adsorption isotherms were constructed using the Freundlich expression (equation 1).

$$q=K_F C^n \qquad (1)$$

In equation 1 (at equilibrium), q is adsorbed analyte in $\mu g\ mg^{-1}$, C is the analyte remaining in solution in $\mu g l^{-1}$, K_F and n are Freundlich adsorption constants representing the adsorption capacity and adsorption coefficient, respectively.

Each adsorption isotherm was carried out in a completely mixed batch reactor (CMBR) stirred with a paddle. The equilibration time of 72h was investigated and found to be sufficient to reach equilibrium for the 74-125 µm fraction. The initial concentrations of atrazine and PSS standard were 10 $\mu g l^{-1}$ (4.6×10^{-8} M) and 5×10^{-7} M respectively, which means that PSS standard was in approximately ten fold excess. PSS standard and atrazine were dissolved in 0.01 M phosphate buffer at pH 6.8 and reference preloaded GAC was added. The amount of GAC ranged from 0.5 to 4.5 mg and the volume was 0.5 l or 1 l.

Adsorption experiments with site-preloaded/reference preloaded GAC

In these experiments the competitive effects for untreated and treated waters through the two treatment plants (Finnsjön and Lackarebäck) were studied. GAC was preloaded in minicolumns with the NOM in the untreated water or treated water for the treatment step under investigation and this GAC is termed site-preloaded. The adsorption experiment was carried out in a CMBR as described previously, with the exception that only one point from the adsorption isotherm was chosen: 1.3 mg of GAC in 0.5 l of water; an initial concentration of atrazine of 10 μgl^{-1} . For each site-preloaded GAC two adsorption experiments were carried out, one with the water used for preloading and one with ultrapure water (DOC < 0.2 mgl^{-1}). As a control the different waters were also tested with the reference preloaded GAC.

Results and Discussion

There is increasing evidence that a low MW fraction of NOM is responsible for preloading and for direct competition with pesticides. Surface water shows two distinct peaks for HPSEC-UV (Figure 1) and a similar profile (although with low signal/noise ratio) appears for HPSEC-fluorescence (Figure 2). The larger fraction is effectively removed, 83% (calculated as integrated %area from the HPSEC chromatograms), after the chemical treatment process. This agrees with the reported removal of dissolved NOM by chemical treatment (flocculation and sedimentation) of between 10% and 90% with an average of approximately 30% (*21*) with the higher removal being correlated to higher MW fractions in the water. This larger fraction, which has been labelled as humic substance (*22*) is therefore readily removed by physico-chemical water treatment processes, but has also been shown to be photochemically degraded (*23*). This fraction was almost absent from the groundwater sample (Figure 3) which verifies the susceptibility to environmental removal processes. The smaller distinct size fraction on the contrary, is present in surface water (Figure 1) and groundwater (Figure 3) and shows only a 11% removal during water treatment. Clearly, this refractory low MW fraction is a candidate NOM fraction for preloading and direct competitive interaction, because the probable small molecular size allows deep micropore penetration. The persistence of this fraction through water treatment processes explains why preloading is observed in GAC columns, even though GAC is frequently the penultimate process before carbonisation/chlorination.

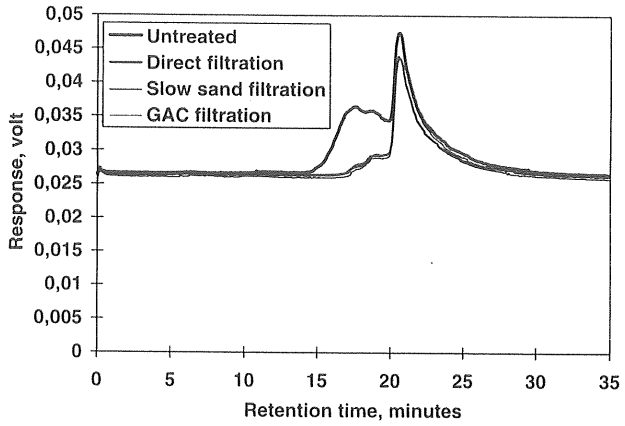


Figure 1 HPSEC-UV chromatograms of NOM in untreated and treated water through Finnsjön treatment plant.

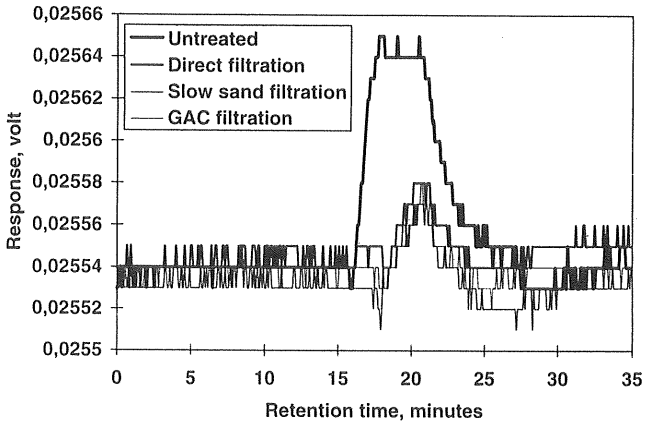


Figure 2 HPSEC-fluorescence chromatograms of NOM in untreated and treated water through Finnsjön treatment plant.

However, evidence from tandem HPSEC-UV-fluorescence (Figures 1 and 2) reveals that the spectral characteristics of this low MW fraction does not remain unchanged through the treatment plant. While abs_{220} (both fractions) is removed by 40%, fluorescence shows a 77% removal. As all fluorescent moeties also contribute to UV absorption, there must be

additional chromophores in the UV-absorbing fraction. Fluorescent molecules tend to be of a highly conjugated nature (*24*), while there are a range of UV-absorbing molecules that are less or not conjugated. The removal of aromatic groups should reduce the effects of preloading on pesticide adsorption to GAC, as Freundlich adsorption isotherms demonstrate the preferential adsorption of these substances to high energy sites (*7,25*) as indicated by the Freundlich heterogeneity parameter n (*26*).

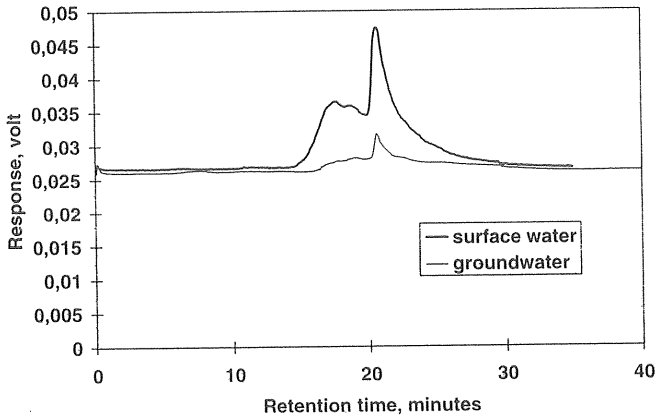
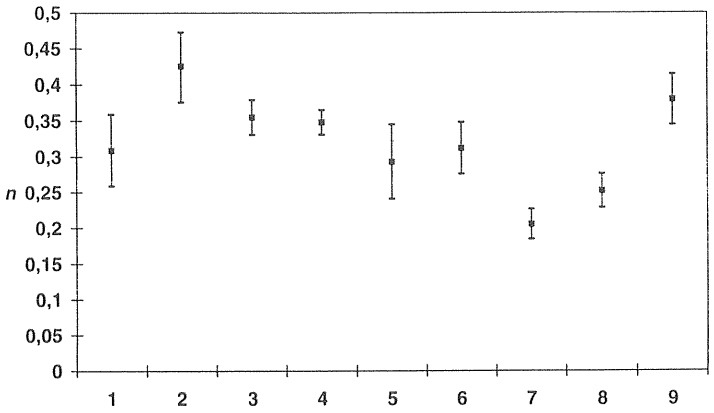


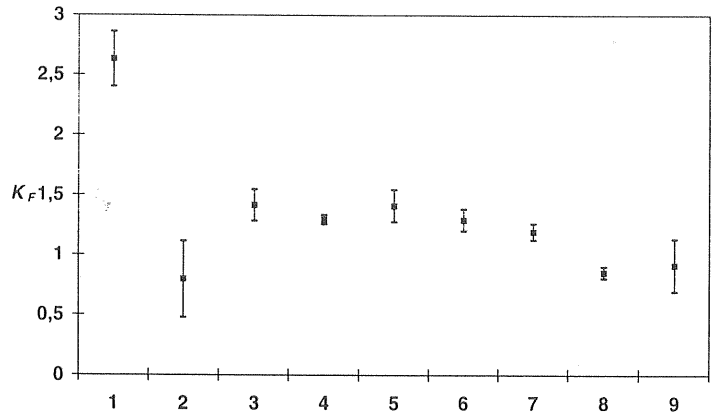
Figure 3 HPSEC-UV in Gräfsnäs groundwater and lake Finnsjön (surface water).

The competitive interaction of atrazine with PSS standards and NOM was investigated at the reference preloaded GAC. The preparation of preloaded GAC for Freundlich adsorption isotherms is difficult, because when the GAC is crushed to allow rapid equilibrium of analyte with adsorption sites, fresh non-preloaded adsorption sites are exposed (*7*). Here GAC was precrushed to the required size range and preloaded in a minicolumn, consequently the preloading effect was retained.

The effect of preloading GAC with NOM and competitive interaction of NOM on atrazine adsorption is revealed through comparison of n values (Figure 4a) and K_F values (Figure 4b). Site energy distribution, as indicated by n, was not significantly affected by preloading with NOM in the minicolumns. It is known that extended preloading can lead to an increase of n towards unity, due to the occupation of high energy sites (*7,25*). This effect is observed for the competitive interaction of Delsjön NOM with atrazine at fresh GAC (Figure 4a). However, the general effect of a competing substance on atrazine adsorption is a reduction of n; this is observed for the low MW PSS standard and Delsjön NOM. The probable mechanism for competitive interaction is that the excess of NOM or PSS 1 430 adsorbs to the whole range of available sites. This leads to a shift to lower n values and also explains the significant reduction of K_F (Figure 4b).



(a)



(b)

No	GAC conditions	Background water
1	Fresh	Ultrapure
2	Fresh	Delsjön
3	Preloaded, reference	Ultrapure
4	Preloaded, reference	PSS 16 800
5	Preloaded, reference	PSS 6 780
6	Preloaded, reference	PSS 4 300
7	Preloaded, reference	PSS 1 430
8	Preloaded, Gräfsnäs	Gräfsnäs
9	Preloaded, Delsjön	Delsjön

Figure 4 Variation of (a) n and (b) K_F with preloading and background competing substance. The 95% confidence intervals are shown with a square representing the mean of four samples.

Although preloading does lead to a lowered K_F value for atrazine in the absence of competing substance (Figure 4b), the effect of a background NOM is always overriding, whether for fresh or preloaded GAC. The PSS 1 430 standard shows a significantly reduced K_F on preloaded GAC, however, both Gräfsnäs and Delsjön NOM show a greater effect on K_F. This finding confirms that the low MW NOM fraction separated by HPSEC is responsible for competition as the PSS standards > 1 430 show no effect. There appears to be no evidence of pore blockage by larger molecules during atrazine adsorption to GAC.

The low DOC concentration for the groundwater (0.55 mgl^{-1}) underlines previous findings for dilution experiments (*20*) that competitive effects are observed down to equimolar concentrations of the target analyte and competitive substances. As target analytes are often at sub-μgl^{-1} (pesticides) and even ngl^{-1} (taste and odour substances such as 2-methylisoborneol) concentrations, competitive effects from NOM would be anticipated even in low NOM groundwater. The question remains whether competitive effects of NOM remain through a water treatment plant.

The competitive interaction of atrazine with NOM was investigated on GAC preloaded in minicolumns. This reference preloaded GAC served as a control with the same preloading conditions for studies of the additional effect of competition of NOM and atrazine through two drinking water treatment plants (WTP), Lackarebäck and Finnsjön. Lackarebäck WTP has the lake Delsjön as water source, whereas Finnsjön WTP extracts water from lake Finnsjön. The results are shown in Figure 5 (Lackarebäck) and Figure 6 (Finnsjön). Ultrapure water illustrates the effect of preloading alone and should be compared to the untreated and treated waters, which show the additional competitive interaction from NOM. For both treatment plants it can be concluded that the extent of competitive interaction is not significantly reduced during water treatment. Low atrazine removal can be attributed to competition with the low MW fraction, which was found by HPSEC to be poorly removed during water treatment (Figure 1).

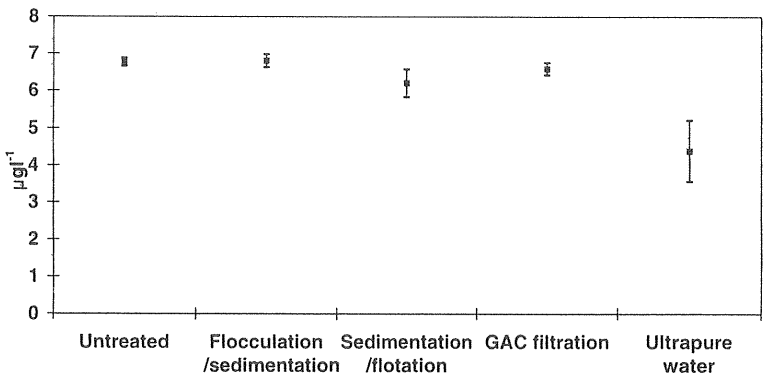


Figure 5 The removal of atrazine (10 μgl^{-1}) through the Lackarebäck WTP, reference preloaded GAC. The 95% confidence intervals are shown with a square representing the mean of four replicates.

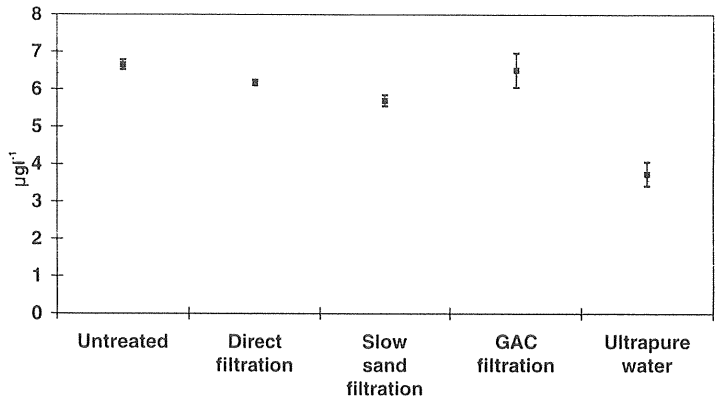


Figure 6 The removal of atrazine (10 $\mu g l^{-1}$) through the Finnsjön WTP, reference preloaded GAC. The 95% confidence intervals are shown with a square representing the mean of four replicates.

The low MW NOM fraction does though, appear to have a significant effect on both the preloading phenomenon and competition during adsorption.The effects of preloading and competitive interaction can be separated by the use of site-preloaded GAC adsorption experiments with ultrapure water and site sampled water (Table 2). In this case the ultrapure water shows the effect of preloading within the treatment plant. The additional effect from competitive interaction is revealed in adsorption experiments where site-preloaded GAC is combined with the site sampled water. The effects from preloading and competitive interaction are slightly elevated for the untreated water from both treatment plants compared to the treated waters but there is no significant difference between the treatments through both WTP's (Table 2). This indicates that the high MW fraction could be responsible for some of the effects from preloading and competitive interaction in untreated water but that the low MW fraction separated by HPSEC, and which is found at all treatment steps, determines both preloading conditions and competitive interaction.

Table 2 Effect of preloading and competitive interaction on atrazine adsorption to site-preloaded GAC through the Lackarebäck WTP and Finnsjön WTP. The table shows mean atrazine concentration of four replicates and the 95% confidence interval in parenthesis. The initial concentration of atrazine was 10 μgl^{-1}.

Treatment plant Site	Site-preloaded GAC Ultrapure water atrazine concentration, μgl^{-1}	Site-preloaded GAC Water at site atrazine concentration, μgl^{-1}
Lackarebäck		
Untreated	3.7 (3.6-3.8)	6.7 (5.9-7.6)
Flocculation/sedimentation	2.8 (2.5-3.2)	5.7 (5.56-5.9)
Sedimentation/flotation	3.5 (3.4-3.6)	5.8 (5.2-6.5)
GAC filtration	3.3 (2.6-4.0)	5.7 (5.1-6.4)
Finnsjön		
Untreated	3.7 (3.4-4.1)	7.2 (6.8-7.7)
Direct filtration	2.4 (2.3-2.5)	6.3 (6.2-6.4)
Slow sand filtration	1.6 (1.6-1.7)	5.8 (5.6-5.9)
GAC filtration	2.2 (2.0-2.3)	5.3 (5.0-5.5)

Clearly, the competitive interaction of NOM with herbicides, has a significant effect on adsorption carried out on preloaded GAC and values reported for distilled water provide an poor overestimation of K_F and n values. Prediction of GAC performance in a treatment plant for herbicide removal therefore requires a consideration of both NOM preloading and NOM competitive interaction. For the most satisfactory prediction the GAC to be used should be precrushed and site-preloaded and adsorption isotherms for target analytes carried out in the presence of the relevant NOM.

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